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V.—ON THE CHEMISTRY OF FISH.

PART I.—ANALYSES OF SPECIMENS OF AMERICAN FISHES.

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The desirability of more information as to the proximate composition of the flesh of fish led to a number of analyses in accordance with the methods described in the chapter on Methods of Analysis. They are very nearly the same as were followed by Almén,[1] who has made a number of analyses of the flesh of fish. His results, with those of Kostytschef, whom I infer to have worked by similar methods, are to be recapitulated in an account of European analyses of fish, to follow.

Table V gives the proportions of proximate ingredients in the water-free substance of the flesh of American fishes as directly determined; that is to say, it recapitulates the determinations of extractive matters, albumen, gelatin, insoluble protein, etc., as made in accordance with the statements in the chapter on Methods of Analysis. The figures for ether extract and ash are those of the previous tables. As there stated, I do not consider the determinations of the nitrogenous constituents entirely accurate. The methods are not yet well enough worked up to give satisfactory results. The figures will, however, serve for comparison with those

[1] Loc. cit.

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obtained by Almén, and, I presume, with those of Kostytschef. It is to be noted, however, that the figures here given refer simply to the flesh, while those of Almén I understand to include the skin with the flesh, and presume that the same may be the case with Kostytschef's, though as to the latter point I am not definitely informed. The last column of Table V gives the sums of the several constituents. These vary more or less from 100 per cent., and thus indicate errors in the determination. Where these footings have varied by more than 5 per cent. from 100 per cent. in the water-free substance (which would correspond to from 1 per cent. to 2 per cent. in the fresh flesh), the insoluble protein for each specimen has been omitted from the table. The methods of estimating the extractive matters, gelatin, and insoluble protein differ in the different specimens with respect to the determinations of ash and fat, as indicated in the table, and stated in full in the details of the analyses which will be given in the monograph already referred to. I have deemed it proper to state the precise facts with reference to these analyses, so that they may be taken exactly for what they are worth. The analytical details will help in judging properly of their value. As stated in the description of the method of analysis, the methods were those laid down by other analysts. We followed those methods and did the work as faithfully as we were able. If the results have no other value, they at least show the need of working up the methods more thoroughly.

Table VI gives the proximate ingredients of the flesh as directly determined. The analyses are those of Table V calculated on fresh substance, the figures for water being those stated in previous tables.

Table VII states the percentages of phosphorus calculated as P_2O_5 and as PO_4, of sulphur as SO_3 and as SO_4, and of chlorine in both water-free substance and fresh substance of flesh. The determinations were made as described in the chapter on Methods of Analysis, and I believe them to be reasonably accurate.

Analyses of preserved fish are given in Tables VIII and IX, and explained in the chapter on Economic Results of Analyses, beyond. The composition of the specimens of fresh and preserved fish as received for analysis, including both flesh and other parts, is stated in Table X and explained in the same chapter.

TABLE V.

Composition of Water-free Substance of Flesh of Specimens of American Fishes. Proximate Ingredients as directly determined.

Kind of Fish.	Laboratory Numbers of Specimens.	Extractive Matters, Cold-water Extract, not coagulated.	Albumen, coagulated from Cold-water Extract.	Gelatin. Hot-water Extract.	Insoluble Protein.	Fats. Ether Extract.	Ash.	Total.
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Black bass	53	10.49[1]	9.54	14.48[1]	...	4.47	5.57	...
Black fish	38	7.46[1]	11.32	15.79[1]	51.00[1]	12.20	5.54	103.31
Common flounder	22	12.77[2]	6.51	24.07[2]	...	5.18	8.63	...
Haddock	21	6.18[2]	7.89	16.36[2]	65.06	0.78	8.72	104.99
Herring	47	4.51[1]	5.23	9.46[1]	...	35.55	4.83	...
Mascalonge	45	9.55[1]	6.95	10.20[1]	56.71[1]	10.70	6.63	100.74
Mackerel	30	8.61[1]	7.27	5.74[1]	47.37[2]	27.04	5.02	101.05
Spanish mackerel	43	6.96[1]	3.92	9.22[1]	...	29.56	4.71	...
White perch	44	6.76[1]	7.35	13.39[1]	..	23.07	4.56	...
"	46	8.88[1]	9.78	11.04[1]	51.47[1]	10.42	5.27	96.86
" Average of 2 specimens.		7.82[1]	8.57	12.22[1]	...	16.75	4.92	...
Pike perch, Wall-eyed pike	52	13.14[1]	5.87	16.98[1]	52.15[1]	2.31	6.75	97.20
Porgy	31	6.35[1]	10.64	7.41[1]	44.40[2]	28.04	4.81	101.65
Red snapper	20	8.38[2]	7.30	16.83[2]	60.84	2.85	5.82	102.02
"	26	8.16[2]	8.12	12.75[2]	56.09	8.58	5.86	99.56
" Average of 2 specimens.		8.27[2]	7.71	14.79[2]	58.46	5.72	5.84	100.79
California salmon	27	4.85[2]	4.21	4.74[2]	32.02	51.59	2.98	100.39
Shad	32	6.68[1]	6.57	6.63[1]	43.60[2]	34.50	4.58	102.56
Sheepshead	48	5.11[1]	7.11	11.98[1]	...	24.02	3.93	...
Smelt	23	16.23[2]	3.02	25.07[2]	37.50	9.76	10.08	101.66
Brook trout	24	11.44[2]	8.01	9.88[2]	55.74	11.61	6.33	103.01
Turbot	49	7.04[1]	0.42	12.89[1]	28.14[1]	50.36	4.47	103.32
Spent Fish.								
Salmon, male	35	9.18[1]	4.69	9.66[1]	53.09[1]	17.66	4.51	98.79
" female	36	6.27[1]	4.59	13.92[1]	...	12.98	5.36	...
" Average of 2 specimens		7.73[1]	4.64	11.79	...	15.32	4.94	...
Land-locked salmon, male	40	9.18[2]	2.94	8.88[1]	...	18.12	5.76	...
" " female	41	10.56[2]	5.14	10.58[1]	...	9.36	5.76	...
" " Average of 2 specimens		9.87[2]	4.04	9.73[1]	...	13.74	5.76	...
Preserved Fish.								
Salt mackerel	42	6.17[1]	0.50	2.91[1]	26.81[1]	39.08	22.76	98.23
Salt cod	34	3.26[1]	1.07	10.38[1]	32.67[1]	0.53	53.82	101.73
"	37	2.50[1]	2.07	7.28[1]	36.92[1]	0.94	52.43	102.14
" Average of 2 specimens		2.88	1.57	8.83	34.80	0.73	53.12	101.94
Boned salt cod	25	7.01[2]	1.84	6.62[2]	32.81	0.71	50.72	99.71
Smoked halibut	28	5.60[2]	1.51	3.23[1]	26.57[2]	31.90	31.01	99.82
Smoked herring	33	13.04[1]	0.48	7.84[1]	33.14[2]	24.18	20.15	98.83
Canned salmon	29	14.21[2]	...	5.27[2]	42.44[2]	32.40	5.24	99.56

[1] Ash- and fat-free. [2] Ash-free.

TABLE VI.

Composition of Flesh of Specimens of American Fishes. Proximate Ingredients as directly determined.

NAMES OF FISH.	Laboratory Numbers of Specimens.	Water.	Extractive Matters. Cold water Extract, not coagulated.	Albumen, coagulated from Cold-water Extract.	Gelatin. Hot-water Extract.	Insoluble Protein.	Fats. Ether Extract.	Ash.	Total.
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Black bass	53	78.61	2.24[1]	2.04	3.10[1]	...	0.96	1.19	...
Black fish	38	76.95	1.72[1]	2.61	3.64[1]	11.76[1]	2.81	1.28	100.77
Common flounder	22	85.04	1.91[2]	0.98	3.60[2]	...	0.77	1.29	...
Haddock	21	82.03	1.11[2]	1.42	2.94[2]	11.70	0.14	1.57	100.91
Herring	47	69.03	1.40[1]	1.62	2.93[1]	...	11.01	1.50	...
Mascalonge	45	76.26	2.27[1]	1.65	2.40[1]	13.46	2.54	1.57	100.15
Mackerel	30	74.14	2.22[1]	1.88	1.48[1]	12.25[2]	6.99	1.30	100.26
Spanish mackerel	43	68.10	2.22[1]	1.25	2.94[1]	...	9.43	1.50	..
White perch	44	75.64	1.65[1]	1.79	3.27[1]	...	5.62	1.11	...
" "	46	75.77	2.22[1]	2.37	2.68[1]	12.47[1]	2.52	1.28	99.31
" " Average of 2 specimens		75.71	1.94[1]	2.08	2.98[1]	...	4.10	1.20	101.24
Pike perch, Wall-eyed pike	52	79.74	2.66[1]	1.19	3.44[1]	10.57[1]	0.47	1.37	99.44
Porgy	31	71.98	1.78[1]	2.98	2.07[1]	12.44[2]	7.86	1.35	100.46
Red snapper	20	78.22	1.81[2]	1.59	3.65[2]	13.25	0.62	1.27	100.41
" "	26	77.34	1.85[2]	1.84	2.89[2]	12.71	1.94	1.33	99.90
" " Average of 2 specimens		77.78	1.83[2]	1.72	3.27[2]	12.98	1.28	1.30	100.15
California salmon	27	62.68	1.81[2]	1.57	1.77[2]	11.95	19.25	1.11	100.14
Shad	32	70.75	1.92[1]	1.92	1.93[1]	12.74[2]	10.08	1.34	100.68
Sheepshead	48	72.01	1.44[1]	1.99	3.36[1]	...	6.72	1.10	...
Smelt	23	80.16	3.22[2]	0.60	4.97[2]	7.44	1.94	2.00	100.33
Brook trout	24	77.54	2.57[2]	1.80	2.22[1]	12.52	2.61	1.42	100.68
Turbot	49	71.39	2.01[1]	0.12	3.69[1]	8.05[1]	14.41	1.28	100.95
SPENT FISH.									
Salmon, male	35	75.27	2.27[1]	1.16	2.89[1]	13.13[1]	4.37	1.12	99.71
" female	36	78.20	1.37[1]	1.00	3.03[1]	...	2.83	1.17	...
" Average of 2 specimens		76.74	1.77	1.08	2.71	...	3.60	1.15	...
Land-locked salmon, male	40	77.88	2.03[2]	0.65	1.97[1]	...	4.01	1.27	...
" " female	41	79.20	2.20[2]	1.07	2.20[1]	...	1.95	1.20	...
" " Average of 2 specimens		78.54	2.11[2]	0.86	2.09[1]	...	2.98	1.24	...
PRESERVED FISH.									
Salt mackerel	42	42.19	3.57[1]	0.29	1.68[1]	15.49[1]	22.59	13.16	98.97
Salt cod	34	53.62	1.51[1]	0.50	4.79[1]	15.15[1]	0.25	24.96	100.78
"	37	53.54	1.16[1]	0.96	3.38[1]	17.17[1]	0.44	24.35	101.00
" Average of two specimens		54.58	1.34	0.73	4.03	16.16	0.35	24.65	100.89
Boned salt cod	25	54.35	3.20[2]	0.84	3.02[1]	14.98	0.32	23.15	99.86
Smoked halibut	28	57.06	2.74[2]	0.74	1.58[1]	13.01[2]	15.61	5.18	99.92
Smoked herring	33	34.55	8.53[1]	0.32	5.13[1]	21.69[2]	15.82	13.19	99.23
Canned salmon	29	65.86	4.85[2]	...	1.80[1]	14.49[2]	11.06	1.79	99.85

[1] Ash- and fat-free.   [2] Ash-free.

TABLE VII.

Percentages of Phosphoric Acid, Sulphuric Acid, and Chlorine in Flesh of Specimens of American Fishes.

Names of Fishes.	Laboratory Number of Specimen.	In Water-free Substance.					In Fresh Substance.				
		Total phosphorus calculated as P_2O_5.	Total phosphorus calculated as PO_4.	Total sulphur calculated as SO_3.	Total sulphur calculated as SO_4.	Chlorine.	Total phosphorus calculated as P_2O_5.	Total phosphorus calculated as PO_4.	Total sulphur calculated as SO_3.	Total sulphur calculated as SO_4.	Chlorine.
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Alewife	5	2.06	2.76	...	...	...	0.50	0.67	...	...	...
Black bass	53	2.04	2.73	4.14	4.97	...	0.44	0.59	0.89	1.07	...
Striped bass	7	2.51	3.36	...	...	...	0.53	0.71	...	...	...
" average of 2 specimens	19	2.16	2.89	2.28	2.73	...	0.44	0.59	0.46	0.55	...
Black fish	38	2.34	3.14	...	...	...	0.48	0.64	...	...	...
Blue fish	12	2.24	3.00	1.97	2.36	1.93	0.52	0.70	0.46	0.55	...
Cod	3	2.93	3.93	...	...	...	0.63	0.84	...	...	0.23
"	11	2.19	2.93	...	...	...	0.36	0.48	...	...	...
" average of 2 specimens		3.18	4.26	...	...	...	0.53	0.71	...	...	...
Eel	14	2.69	3.60	...	...	1.03	0.45	0.60	...	...	...
Flounder	2	1.70	2.28	...	...	...	0.51	0.68	...	...	...
"	22	1.86	2.49	2.23	2.68	...	0.31	0.41	0.38	0.46	...
" average of 2 specimens		2.70	3.62	3.10	3.72	...	0.40	0.54	0.46	0.55	...
Haddock	16	2.28	3.06	2.67	3.20	...	0.36	0.48	0.42	0.50	...
"	21	2.43	3.26	2.26	2.71	...	0.48	0.64	0.40	0.48	...
" average of 2 specimens		2.54	3.40	...	...	...	0.45	0.60	...	...	...
Halibut	1	2.49	3.34	...	...	...	0.47	0.63	0.44	0.53	...
"	9	2.11	2.83	2.11	2.53	...	0.44	0.59	...	...	...
" average of 2 specimens		1.51	2.02	...	...	...	0.43	0.58	...	...	...
Herring	47	1.81	2.43	1.77	2.12	...	0.55	0.74	0.55	0.66	...
" average of 2 specimens		1.77	2.37	...	...	...	0.52	0.70	...	...	...
Mascalonge	45	2.21	2.96	1.55	1.86	...	0.52	0.70	0.37	0.44	...
Mackerel	8	2.26	3.03	...	...	...	0.47	0.63	...	...	...
"	13	2.43	3.26	...	...	...	0.63	0.84	...	...	...
"	30	2.16	2.89	...	...	...	0.56	0.75	...	...	...
"	39	1.60	2.14	1.68	2.02	0.68	0.58	0.78	0.43	0.52	...
" average of 4 specimens		2.11	2.83	...	...	...	0.56	0.75	...	...	...
Spanish mackerel	43	1.88	2.52	...	...	...	0.60	0.80	...	...	0.24
White perch	44	1.46	1.96	2.54	3.05	...	0.36	0.48	0.62	0.74	...
"	46	2.13	2.85	2.80	3.36	...	0.52	0.70	0.68	0.82	...
" average of 2 specimens		1.79	2.40	2.67	3.20	...	0.44	0.59	0.65	0.78	...
Pike perch	52	2.24	3.00	4.43	5.32	...	0.45	0.60	0.90	1.08	...

TABLE VII.—Concluded.

Names of Fishes	Laboratory Number of Specimen	Water-free — Total phosphorus as P_2O_5 (per ct.)	Water-free — Total phosphorus calculated as PO_4 (per ct.)	Water-free — Total sulphur calculated as SO_3 (per ct.)	Water-free — Total sulphur calculated as SO_4 (per ct.)	Water-free — Chlorine (per ct.)	Fresh — Total phosphorus as P_2O_5 (per ct.)	Fresh — Total phosphorus calculated as PO_4 (per ct.)	Fresh — Total sulphur calculated as SO_3 (per ct.)	Fresh — Total sulphur calculated as SO_4 (per ct.)	Fresh — Chlorine (per ct.)
Porgy ……	15	3.04	4.07				0.62	0.83			
" average of 2 specimens ……	31	1.98	2.65	1.84	2.21		0.56	0.75	0.52	0.62	
Red snapper……	20	2.51	3.36				0.59	0.79			
" ……	26	2.15	2.88				0.47	0.63			
" average of 2 specimens……		2.10	2.81	2.19	2.63		0.48	0.64	0.47	0.56	
Salmon……	14	2.13	2.85	2.06	2.47		0.47	0.63	0.46	0.55	
" ……	27	1.79	2.40	2.13	2.56		0.59	0.79	0.47	0.56	
Spent salmon, male……	35	1.86	2.49	1.14	1.37	0.74	0.69	0.92	0.43	0.52	0.18
" female……	36	1.89	2.53	1.58	1.90	0.85	0.47	0.63	0.39	0.47	0.18
" average of 2 specimens……		2.20	2.95	1.45	1.74	0.80	0.48	0.64	0.32	0.38	0.18
Spent salmon, land-locked, male……	40	2.05	2.75	1.52	1.82	0.95	0.48	0.64	0.36	0.43	0.21
" " female……	41	2.31	3.10	1.77	2.12	0.93	0.51	0.68	0.39	0.47	0.19
" " average of 2 specimens……		2.43	3.26	1.98	2.38	0.94	0.51	0.68	0.41	0.49	0.20
Shad……	10	2.37	3.18	1.88	2.26		0.51	0.68	0.40	0.48	
" ……	32	1.94	2.60				0.67	0.90			
" average of 2 specimens……		1.76	2.36	1.78	2.14	0.74	0.52	0.70	0.52	0.62	0.22
Sheepshead……	48	1.85	2.48				0.60	0.80			
" average of 2 specimens……		1.62	2.17	1.71	2.05		0.45	0.60	0.48	0.58	
Smelt ……	23	4.10	5.49	2.79	3.35		0.81	1.08	0.55	0.66	
Turbot……	49	1.66	2.22	1.12	1.34		0.48	0.64	0.32	0.38	
Lake trout……	17	1.80	2.41	1.94	2.33		0.56	0.75	0.62	0.74	
Brook trout……	24	2.72	3.64	2.13	2.56		0.61	0.82	0.48	0.58	
White fish……	18	2.35	3.15	1.36	1.63		0.71	0.95	0.41	0.49	
PRESERVED FISH.											
Salt mackerel……	42	0.61	0.82	1.06	1.27	25.66	0.35	0.47	0.61	0.73	11.90
Salt cod……	34	0.61	0.82	1.56	1.87	25.71	0.28	0.37	0.72	0.86	11.94
" ……	37	0.48	0.64	1.61	1.93	25.69	0.22	0.29	0.75	0.90	11.92
" average of 2 specimens……		0.55	0.74	1.59	1.91	24.51	0.25	0.34	0.74	0.89	11.19
Boned salt cod ……	25	0.79	1.06	1.48	1.78	17.69	0.36	0.48	0.68	0.82	8.66
Smoked halibut……	28	0.95	1.27	0.89	1.07	11.01	0.46	0.62	0.44	0.53	7.21
Smoked herring……	33	1.28	1.72	1.89	2.27		0.84	1.12	1.24	1.49	
Canned salmon……	29	1.77	2.37	1.27	1.52		0.60	0.80	0.43	0.52	

OTHER ANALYSES OF AMERICAN FISHES.

Prof. R. H. Chittenden has reported an analysis of the flesh of halibut, " a fresh sample obtained in the market."[1] The source of the specimen, the season in which it was taken, and the portion of the body used for analysis are not stated. It appears, however, to have been rather lean in comparison with the specimens of halibut above reported. To facilitate such comparison, I give the result in the forms followed in the tables here, basing the calculation on the averages of Prof. Chittenden's analyses, which from their close agreement, as well as from the context, I take to be duplicate determinations of the same specimen of flesh.

Composition of Flesh of Halibut.

In water-free substance ("flesh dried at 100° C.")

Nitrogen.	Protein, $N \times 6.25$.	Fats.	Ash.	Protein ($N \times 6.25$) + Fats + Ash.	Albuminoids, etc., by difference.
per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
11.68	73.00	7.12	6.35	86.47	86.53

In flesh ("fresh sample.")

Water.	Water-free substance.	Albuminoids, etc., by difference.	Fats.	Ash.	Nitrogen.	Protein, $N \times 6.25$.	Water + Protein ($N \times 6.25$) + Fats + Ash.
per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
82.88	17.12	14.77	1.27	1.08	2.01	12.56	97.79

The flesh in the fresh condition contained 0.37 per cent. of phosphorus. For the other details of the analyses there is scarcely place here.

Prof. G. H. Cook has reported an analysis of menhaden, *Brevoortia tyrannus*,[2] which was, however, made for the purpose of learning the value of the fish for fertilising the soil, and yielded no data that could well be utilised here. No other analyses of flesh of American food-fishes have come to my attention.

The limits of the present account and the desirability of reference to some of the other branches of the investigation and to

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[1] Am. Jour. Sci. [3], **13**, 123.   [2] Geology of New Jersey, p. 498.

work in other similar lines, preclude detailed discussion of the analyses here. I will, however, call attention to a few facts and generalisations from them.

IV.—CLASSIFICATION OF FISH BY THEIR COMPOSITION.

On the basis of the figures of Tables I, III, and X, I have attempted a classification of the specimens of American fish analysed, by their content of (1) flesh, (2) water-free substance in flesh, and (3) water and fats. With the following figures, the classifications will need no further explanation. Where more than one specimen was analysed the averages of the analyses are used. Of course, a satisfactory classification would require many more analyses. Nevertheless, these figures may be assumed to give a tolerably fair idea of the relative composition of the fish, or at least an approximation that may serve until more complete data are obtained. Accordingly, the exact order of the species in each of the groups in Tables XI, XII, and XIII must be regarded as by no means fixed, since further analyses would very likely give averages varying more or less from the results here tabulated.

In Table XI, the species of which entire specimens of fish were received for analysis, i. e. specimens from which no portion had been removed before weighing and preparing for analysis, are arranged in order from those with the largest to those with the smallest proportions of flesh. The data are from Tables I and X.

TABLE XI.

Classification of Fish by percentages of Flesh, chiefly Muscular Tissue, in Entire Body.

Species containing 60 per cent. or over of Flesh.

Number of specimens analysed.	Kinds of Fish.	Flesh.	Number of specimens analysed.	Kinds of Fish.	Flesh.
1	Spanish mackerel...	p. ct 65.4	1	Red snapper....................	p. ct. 60.0
4	Salmon...	64.7			

TABLE XI.—*Continued.*

Species containing between 60 and 50 per cent. of Flesh.

Number of specimens analysed.	Kinds of Fish.	Flesh.	Number of specimens analysed.	Kinds of Fish.	Flesh.
2	Smelt...........................	58.1	1	Herring..........................	54.0
1	Pike (pickerel.)...............	57.3	2	Pickerel........................	52.9
1	Cisco.........................	57.3	2	Spent land-locked salmon.....	52.7
1	Butter fish	57.2	1	Turbot.........................	52.3
2	Spent salmon.................	56.4	3	Brook trout	51.9
5	Mackerel......................	55.4	1	Mascalonge....................	50.8
2	Pompano	54.5	2	Alewife........................	50.5
1	Lamprey eel	54.2			

Species containing between 50 and 40 per cent. inclusive, of Flesh.

7	Shad	49.9	1	Winter flounder.	43.8
1	Weak fish.....................	48.1	1	Lake trout, "Mackinaw trout."	43.7
2	Cod..........................	47.5	1	King fish.....................	43.4
1	White fish	46.5	1	Pike perch, "Wall-eyed pike."	42.8
1	Small-mouthed black bass	46.4	1	Mullet........................	42 1
5	Striped bass..................	45.1	1	Tom-cod......................	40.1
1	Large-mouthed black bass	44.0	3	Porgy........................	40.0
1	Sea bass.....................	43.9			

Species containing between 40 and 30 per cent. of Flesh.

2	Black fish....................	39.9	1	Red bass,.....................	36.5
2	White perch	37.5	1	Sheepshead...................	34.0
1	Yellow perch..	37.3	1	Common flounder.............	33.2
1	Pike perch, Gray pike.....	36.8			

In Table XII, compiled from Table III, the species are grouped by the percentages of water-free substance in the flesh, from those with the most to those with the least water-free substance. Of course, those with the most water-free substance have the least water, and vice versa; hence the first in the list have the lowest percentages of water, and the last are the most watery.

TABLE XII.

Classification of Fish by Proportions of Water-free Substance in Flesh of Specimens Analysed.

Species containing over 30 per cent. of water-free substance.

Number of specimens analysed.	Kinds of Fish.	Water-free substance.	Number of specimens analysed.	Kinds of Fish.	Water-free substance.
		p. ct			p. ct.
2	California salmon............	36.4	1	Herring	31.0
5	Salmon......................	36.4	2	Lake trout...................	30.9
1	Spanish mackerel.	31.9	1	White fish...................	30.2

TABLE XII.—*Continued.*

Species containing from 30 to 25 per cent. inclusive, of water-free substance.

Number of specimens analysed.	Kinds of Fish.	Water free substance.	Number of specimens analysed.	Kinds of Fish.	Water free substance.
		p. ct			
1	Butter fish	30.0	6	Mackerel..........	26.6
7	Shad........	29.4	2	Alewife........	25.6
1	Lamprey eel........	28.9	1	Small-mouthed black bass...	25.2
1	Turbot........	28.6	1	Mullet........	25.1
2	Salt-water eel........	28.4	3	Porgy	25.0
2	Pompano.......	27.2			

Species containing between 25 and 20 per cent. of water-free substance.

3	Halibut.........	24.6	1	Large-mouthed black bass...	21.4
2	Sheepshead	24.5	1	Sturgeon.	21.3
2	White perch.........	24.3	1	Weak fish........	21.0
1	Pollock	24.0	4	Black fish......	20.9
1	Cisco..........	23.9	2	Smelt.........	20.8
1	Mascalonge..........	23.7	1	King fish.	20.8
2	Spent salmon........	23.3	2	Yellow perch.	20.8
6	Striped bass.........	22.3	1	Sea bass.........	20.7
3	Brook trout	22.3	2	Grouper.........	20.6
1	Blue fish...	21.5	2	Pickerel	20.3
3	Red snapper.........	21.5	1	Pike perch, Wall-eyed pike.	20.3
2	Spent land-locked salmon..	21.5	1	Pike pickerel	20.2
1	Small-mouthed red horse ...	21.4			

Species containing between 20 and 15 per cent. of water-free substance.

1	Pike perch, Gray pike.......	19.2	1	Skate	17.9
1	Tom-cod..........	18.5	5	Cod	17.4
1	Red bass..........	18.4	1	Hake......	16.9
4	Haddock	18.3	2	Common flounder..	15.8
1	Cusk.........	18.0	1	Winter flounder.	15.7

Table XIII, likewise from Table III, gives a grouping of the species by the proportions of fat (ether extract) in the specimens analysed. They are arranged in order from those with the most to those with the least fat in the flesh. The proportions of water are also given to illustrate the principle, to be discussed in another place, that, as a rule, the percentage of water in the muscular tissue diminishes as that of fat increases, and vice versa. In general the fattest species have the most water-free substance.

TABLE XIII.

Classification of Fish by Proportions of Fat in Flesh of Specimens Analysed.

Species containing over 5 per cent. of Fats.

Number of specimens analysed.	Kinds of Fish.	Water.	Fats.	Number of specimens analysed.	Kinds of Fish.	Water.	Fats.
		p. ct.	p. ct.			p. ct.	p. ct.
2	California salmon	63.6	17.9	1	Spanish mackerel	68.1	9.4
1	Turbot	71.4	14.4	2	Salt-water eel	71.6	9.1
5	Salmon	63.6	13.4	2	Pompano	72.8	7.6
1	Lamprey eel	71.1	13.3	6	Mackerel	73.4	7.1
2	Lake trout	69.1	11.4	1	White fish	69.8	6.5
1	Butter fish	70.0	11.0	3	Halibut	75.4	5.2
1	Herring	69.0	11.0	3	Porgy	75.0	5.1
7	Shad	70.6	9.5				

Species containing between 5 and 2 per cent. of Fats.

2	Alewife	74.4	4.9	6	Striped bass	77.7	2.8
1	Mullet	74.9	4.6	1	Mascalonge	76.3	2.5
2	White perch	75.7	4.1	1	Small-mouthed black bass.	74.8	2.4
2	Sheepshead	75.6	3.7	1	Weak fish	79.0	2.4
2	Spent salmon	76.7	3.6	1	Small-mouthed red horse	78.6	2.4
1	Cisco	76.2	3.5	3	Brook trout	77.7	2.1
2	Spent land-locked salmon	78.5	3.0				

Species containing less than 2, the majority less than 1 per cent. of Fats.

1	Sturgeon	78.7	1.9	2	Common flounder	84.2	0.7
2	Smelt	79.2	1.8	2	Grouper	79.4	0.6
1	Skate	82.2	1.4	1	Pike pickerel	79.8	0.6
4	Black fish	79.1	1.4	1	Sea bass	79.3	0.5
1	Blue fish	78.5	1.3	1	Pike perch, Wall-eyed pike	79.7	0.5
3	Red snapper	78.5	1.0	2	Pickerel	79.7	0.5
1	Large-mouthed black bass.	78.6	1.0	1	Red bass	81.6	0.5
1	King fish	79.2	1.0	1	Tom-cod	81.6	0.4
1	Pollock	76.0	0.8	5	Cod	82.6	0.4
2	Yellow perch	79.3	0.8	1	Winter flounder	84.4	0.4
1	Pike perch, Gray pike	80.9	0.8	4	Haddock	81.7	0.3
1	Hake	83.1	0.7	1	Cusk	82.0	0.2

Comparison of the above groupings with the classification by families as practised by ichthyologists shows no very definite connection between the two. For that matter there is perhaps no reason to expect any such connection.

TABLE VIII.

Composition of Water-free Substance of Flesh of American Specimens of Preserved Fish.

KIND OF FISH.	Laboratory Numbers of Specimens.	Nitrogen.	Protein, N × 6.25	Fats, Ether Extract.	Crude Ash (including Salt).	Protein (N × 6.25) + Fats + Ash.	Albuminoids, etc. (by difference).
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
DRIED.							
Desiccated cod......	79	14.72	92.00	2.24	9.78	104.02	87.98
SALTED.							
Mackerel.........	42	5.85	36.56	39.08	22.76	98.40	38.16
SALTED AND DRIED.							
Cod......	34	8.58	53.63	0.53	53.82	107.98	45.65
"	37	8.91	55.69	0.94	52.43	109.06	46.63
" boned......	25	9.20	57.50	0.71	50.72	108.93	48.57
Desiccated cod......	80	13.04	81.50		5.54	13.40	100.44	81.06
SALTED, SMOKED AND DRIED.							
Haddock......	88	13.58	84.88	0.62	13.10	98.60	86.28
Halibut......	28	6.04	37.75	31.90	31.01	100.66	37.09
"	218	7.04	44.00	27.61	28.42	100.03	43.97
Herring	33	9.03	56.44	24.18	20.15	100.77	55.67
CANNED.							
Mackerel.........	94	9.87	61.68	27.28	10.17	99.13	62.55
Salmon......	29	9.87	61.69	32.40	5.24	99.33	62.36
"	96	8.48	53.00	38.55	9.34	100.89	52.11
"	241	7.34	45.88	50.62	4.15	100.65	45.23
Sardines[1]......	87	9.12	57.00	29.14	12.85	98.99	58.01
Tunny, "Horse mackerel"	240	12.72	79.50	14.84	6.19	100.53	78.97
Salt mackerel......	55	4.68	29.25	49.22	21.09	99.56	29.69
" "	219	5.08	31.75	44.05	24.53	100.33	31.42
Smoked haddock......	275	11.40	71.25	7.18	23.14	101.57	69.68

V.—ECONOMIC RESULTS OF ANALYSES.

As the object of the United States Fish Commission, at whose instance the present investigation was undertaken, was to obtain information of economic as well as purely scientific value, a number of analyses were made of the flesh of prepared fish. A few of the figures obtained were given in Tables IV, V, and VI. The principal results are included in Tables VIII and IX, which give data for the flesh of preserved fish similar to those for the flesh in its

[1] This specimen was, or at least purported to be, from France.

natural condition in Tables II and III. Although their value rests mainly upon what they show of the nutritive values, the replacement of the water in the flesh by salt is a matter of physiological interest. To estimate the percentage of salt, the total ash was determined, and the quantity properly belonging to the flesh calculated by assuming that its ratio to the sum of nitrogenous matters and fat would be the same as in the specimens of unsalted flesh of the same species. The mineral matter thus computed was subtracted from the total ash and the remainder taken as representing the amount of salt.

Table X gives the composition of the specimens of fish as received for analysis, including both flesh and refuse matters. The figures are computed from Tables I, III, and IX, the percentages of refuse and of constituents of flesh serving as the basis for the calculations. The figures for nitrogenous substances are reckoned by difference as explained in the discussion of Tables II and III. Deductions from these tables, concerning the nutritive values of fish, are to be given in the monograph referred to.

Composition of Flesh of American Specimens of Preserved Fish.

Kind of Fish.	Laboratory Numbers of Specimens.	Water.	Water-free Substance.	Albuminoids, etc. (by difference).	Fats. Ether Extract.	Ash +.	Salt +.	Nitrogen.	Protein, N × 6.25.	Water + Protein (N × 6.25) + Fats + Ash + Salt.
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
DRIED.										
Desiccated cod, "Evaporated fish"[1]	79	15.25	81.87	74.56	1.90	5.41	2.88	12.48	77.97	103.41
SALTED.										
Mackerel	42	42.19	47.21	22.06	22.59	2.56	10.60	3.38	21.14	99.08
SALTED AND DRIED.										
Cod	34	53.62	23.01	21.17	0.25	1.59	23.37	3.98	24.87	103.70
"	37	53.54	23.75	21.67	0.44	1.64	22.71	4.14	25.86	104.19
" Average of 2 specimens		53.58	23.38	21.42	0.34	1.62	23.04	4.06	25.37	103.95
Boned cod, "Boneless codfish"	25	54.35	24.17	22.18	0.32	1.67	21.48	4.20	26.25	104.07
Desiccated cod, "Evaporated Fish"[1]	80	11.65	81.75	71.62	4.89	5.24	6.60	11.52	72.02	100.40
SALTED, SMOKED AND DRIED.										
Haddock	88	72.56	25.38	23.68	0.17	1.53	2.06	3.73	23.29	99.61
Halibut	28	51.06	35.89	18.15	15.61	2.13	13.05	2.96	18.49	100.34
"	218	47.70	39.43	23.00	14.44	1.99	12.87	3.68	23.01	100.01
" Average of 2 specimens		49.38	37.66	20.57	15.03	2.06	12.96	3.32	20.75	100.18
Herring	33	34.55	53.79	36.44	15.82	1.53	11.66	5.91	36.94	100.50
CANNED.										
Mackerel	94	68.18	29.89	19.91	8.68	1.30	1.93	3.14	19.63	99.72
Salmon	29	65.86	33.61	21.29	11.06	1.26	0.53	3.37	21.06	99.77
"	96	62.23	35.58	19.69	14.55	1.34	2.19	3.20	20.02	100.33
"	241	57.55	42.04	19.20	21.49	1.35	0.41	3.12	19.47	100.27
" Average of 3 specimens		61.88	37.08	20.06	15.70	1.32	1.04	3.23	20.18	100.12
Sardines[2]	87	56.37	43.63	25.31	12.71	5.61	...	3.98	24.87	99.56
Tunny	240	72.74	27.26	21.52	4.05	1.69	...	3.47	21.67	100.15
Salt mackerel	95	43.23	47.33	16.36	27.94	2.53	9.44	2.66	16.60	99.74
"	219	43.62	45.22	17.71	24.84	2.67	11.16	2.86	17.90	100.19
" Average of 2 specimens		43.43	46.27	17.28	26.39	2.60	10.30	2.76	17.35	99.97
Smoked haddock	275	68.73	25.68	21.78	2.25	1.65	5.50	3.58	22.29	100.51

TABLE X.

Composition of American Fishes. Specimens as received for Analysis, including both Flesh (Edible Portion) and Refuse.

Names of Fish and Portions Analysed.	Laboratory Numbers of Specimens.	Refuse: Entrails, Bones, Skin, etc.	Edible Portion. Flesh.	Edible Portion. Water.	Edible Portion. Water-free Substance (Nutrients).	Edible Portion. Nutrients. Albumin-oids (by difference).	Edible Portion. Nutrients. Fats.	Edible Portion. Mineral Matters.
		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Fresh Fish.								
Sturgeon, section of anterior part of body	238	14.4	85.6	67.4	18.2	15.4	1.6	1.2
Small-mouthed red horse, entrails removed	258	52.5	47.5	37.3	10.2	8.5	1.1	0.6
Herring, whole	47	46.0	54.0	37.3	16.7	10.0	5.9	0.8
Alewife, whole	5	49.5	50.5	38.3	12.2	9.5	1.9	0.8
" whole	220	49.4	50.6	36.9	13.7	9.9	3.0	0.8
" " Average of 2 specimens		49.5	50.5	37.5	13.0	9.7	2.5	0.8
Shad, whole	6	49.3	50.7	35.3	15.4	9.2	5.5	0.7
" "	10	46.4	53.6	35.0	18.6	10.5	7.3	0.8
" "	32	45.9	54.1	38.3	15.8	9.6	5.5	0.7
" "	212	44.4	55.6	39.5	16.1	9.9	5.7	0.5
" "	221	53.2	46.8	33.7	13.1	9.3	3.1	0.7
" "	245	52.7	47.3	34.1	13.2	8.6	3.8	0.8
" "	249	58.8	41.2	30.3	10.9	7.4	2.9	0.6
" " Maximum of 7 specimens		58.8	55.6	39.5	18.6	10.5	7.3	0.8
" " Minimum " "		44.4	41.2	30.3	10.9	7.4	2.9	0.6
" " Average		50.1	49.9	35.2	14.7	9.2	4.8	0.7
Smelt, whole	23	34.8	65.2	52.3	12.9	10.4	1.2	1.3
" "	207	49.0	51.0	39.9	11.1	9.6	0.8	0.7
" " Average of 2 specimens		41.9	58.1	46.1	12.0	10.0	1.0	1.0
White fish, whole	18	53.5	46.5	32.5	14.0	10.3	3.0	0.7
Cisco, whole	111	42.7	57.3	43.6	13.7	11.0	2.0	0.7
Calfornia salmon, sections of anterior part of body	27	0.0	100.0	62.7	37.3	17.0	19.2	1.1
" " " "	233	10.3	89.7	57.9	31.8	16.1	14.8	0.9
" " " Av. of 2 specimens		5.2	94.8	60.3	34.5	16.5	17.0	1.0
Salmon, female, whole	77	33.5	66.5	42.2	24.3	13.3	10.0	1.0
" "	78	30.8	69.2	45.0	24.2	13.9	9.3	1.0
" "	279	37.5	62.5	38.3	21.2	15.2	8.1	0.9

TABLE X.—Continued.

Names of Fish and Portions Analysed	Laboratory Numbers of Specimens	Refuse: Entrails, Bones, Skin, etc. per cent	Edible Portion. Flesh per cent	Water per cent	Water-free Substance (Nutrients) per cent	Albumin-oids (by difference) per cent	Fats per cent	Mineral Matters per cent
Salmon, male, whole	280	39.5	60.5	36.9	23.6	14.8	7.9	0.9
" whole. Maximum of 4 specimens		39.5	69.2	45.0	24.3	15.2	10.0	1.0
" " Minimum " "		30.8	60.2	36.9	23.6	13.3	7.9	0.9
" " Average " "		35.3	64.7	40.6	24.1	14.3	8.8	1.0
" entrails removed		23.8	76.2	51.2	25.0	14.6	9.5	0.9
Lake trout, "Mackinaw trout," whole	14	56.3	43.7	30.0	13.7	7.7	5.4	0.6
" " entrails removed	17	35.2	64.8	45.0	19.8	12.4	6.6	0.8
Brook trout, whole, cultivated	255	50.1	49.9	38.7	11.2	9.2	1.3	0.7
" "	24	45.2	54.8	43.8	11.0	10.1	0.4	0.5
" "	254	49.1	50.9	38.6	12.3	10.2	1.5	0.6
" " Average of 3 specimens	256	48.1	51.9	40.4	11.5	9.8	1.1	0.6
Pickerel, whole	100	45.4	54.6	43.6	11.0	10.0	0.3	0.7
" "	224	48.7	51.3	40.8	10.5	9.7	0.2	0.6
" " Average of 2 specimens		47.1	52.9	42.2	10.7	9.8	0.2	0.7
Pike (pickerel), whole	98	42.7	57.3	45.7	11.6	10.7	0.3	0.6
Mascalonge, whole	45	49.2	50.8	38.7	12.1	10.0	1.3	0.8
Eel, salt-water, skin, head and entrails removed	4	21.4	78.6	54.9	23.7	14.9	8.1	0.7
" " " " Av. of 2 specimens	217	19.0	81.0	59.4	21.6	14.3	6.4	0.9
" " " " "		20.2	79.8	57.2	22.6	14.6	7.2	0.8
Mullet, whole	126	57.9	42.1	31.5	10.6	8.1	2.0	0.5
Mackerel, whole	8	38.3	61.7	48.5	13.2	11.2	1.4	0.6
" "	13	51.8	48.2	35.8	12.4	8.4	3.4	0.6
" "	30	48.9	51.1	37.9	13.2	8.9	3.6	0.7
" "	39	33.8	66.2	42.4	23.8	12.1	10.7	1.0
" "	261	50.4	49.6	37.4	12.2	9.5	2.1	0.6
" Maximum of 5 specimens		57.9	66.2	48.5	23.8	12.1	10.7	1.0
" Minimum " "		33.8	48.2	35.8	12.2	8.4	1.4	0.6
" Average " "		44.6	55.4	40.4	15.0	10.0	4.3	0.7
" entrails removed	230	40.7	59.3	43.7	15.6	11.4	3.5	0.7

Table X.—Continued.

Names of Fish and Portions Analysed	Laboratory Numbers of Specimens	Refuse: Entrails, Bones, Skin, etc.	Edible Portion. Flesh.	Edible Portion. Water.	Water-free Substance. (Nutrients.)	Albuminoids (by difference).	Nutrients. Fats.	Mineral Matters.
		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Pompano, whole	234	42.4	57.6	38.8	18.8	10.5	7.8	0.5
" "	263	48.6	51.4	40.2	11.2	9.9	0.8	0.5
" " Average of 2 specimens		45.5	54.5	39.5	15.0	10.2	4.3	0.5
Blue fish, entrails removed	12	48.6	51.4	40.3	11.1	9.8	0.6	0.7
Butter fish, whole	90	42.8	57.2	40.1	17.1	10.2	6.3	0.6
Black bass (large-mouthed), whole	53	56.0	44.0	34.6	9.4	8.5	0.4	0.5
" " (small-mouthed), "	91	53.6	46.4	34.7	11.7	10.0	1.1	0.6
Yellow perch, whole	127	62.7	37.3	30.0	7.3	6.7	0.2	0.4
" " head, entrails, fins and tail removed	208	35.1	64.9	50.7	14.2	12.6	0.7	0.9
Wall-eyed pike, whole	52	57.2	42.8	34.1	8.7	7.9	0.2	0.6
Gray pike, whole	257	63.2	36.8	29.7	7.1	6.4	0.3	0.4
Striped bass, whole	7	56.7	43.3	34.2	9.1	7.9	0.7	0.5
" "	19	56.9	43.1	34.4	8.7	7.2	0.9	0.6
" "	225	48.6	51.4	39.7	11.7	9.7	1.4	0.6
" "	237	57.1	42.9	32.5	10.4	8.3	1.6	0.5
" "	248	55.4	44.6	34.7	9.9	8.4	1.0	0.5
" " Maximum of 5 specimens		57.1	51.4	39.7	11.7	9.7	1.6	0.6
" " Minimum " "		48.6	42.9	32.5	8.7	7.2	0.7	0.5
" " Average " "		54.9	45.1	35.1	10.0	8.3	1.1	0.6
" " entrails removed	260	51.2	48.8	37.4	11.4	8.7	2.2	0.5
White perch, whole	44	63.2	36.8	27.8	9.0	6.5	2.1	0.4
" " "	46	61.8	38.2	28.9	9.3	7.8	1.0	0.5
" " " Average of 2 specimens		62.5	37.5	28.4	9.1	7.2	1.5	0.4
Sea bass, whole	251	56.1	43.9	34.8	9.1	8.3	0.2	0.6
Red grouper, entrails removed	114	55.8	44.2	35.3	8.9	8.2	0.2	0.5
" " "	271	55.9	44.1	34.8	9.3	8.5	0.3	0.5
" " " Average of 2 specimens		55.9	44.1	35.0	9.1	8.4	0.2	0.8
Red snapper, whole	20	40.0	60.0	46.9	13.1	12.0	0.4	0.6
" " entrails removed	26	52.5	47.5	36.8	10.7	9.2	0.9	0.6
" " entrails and gills removed	242	45.3	54.7	43.7	11.0	10.0	0.3	0.7
" " dressed. Average of 2 specimens		48.9	51.1	40.3	10.8	9.6	0.6	0.6

2

TABLE X.—Continued.

Names of Fish and Portions Analysed.	Laboratory Numbers of Specimens.	Refuse: Entrails, Bones, Skin, etc. per cent.	Edible Portion Flesh. per cent.	Water. per cent.	Water-free Substance. (Nutrients.) per cent.	Albumin-oids (by difference). per cent.	Fats. per cent.	Mineral Matters. per cent.
Porgy, whole...........................	15	65.1	34.9	27.8	7.1	6.1	0.5	0.5
" "	31	57.3	42.7	30.7	12.0	8.0	3.4	0.6
" "	262	57.6	42.4	31.1	11.3	8.2	2.5	0.6
" " Maximum of 3 specimens.......		65.1	42.7	31.1	12.0	8.2	3.4	0.6
" " Minimum " "		57.3	34.9	27.8	7.1	6.1	0.5	0.5
" " Average " "		60.0	40.0	29.9	10.1	7.4	2.1	0.6
Sheepshead, entrails removed.......	48	56.5	43.5	31.3	12.2	8.8	2.9	0.5
" whole..........................	250	66.0	34.0	26.9	7.1	6.4	0.2	0.5
Red bass, whole.....................	270	63.5	36.5	29.8	6.7	6.1	0.2	0.4
King fish, "	252	56.6	43.4	34.4	9.0	8.1	0.4	0.5
Weak fish, "	273	51.9	48.1	38.0	10.1	8.4	1.1	0.6
Black fish, "	38	56.2	43.8	33.7	10.1	8.3	1.2	0.6
" " entrails removed..........	205	64.1	35.9	29.2	6.7	6.3	0.2	0.2
" " "	244	57.8	42.2	33.5	8.7	7.9	0.4	0.4
" " "	269	53.6	46.4	36.4	10.0	8.7	0.7	0.6
" " whole. Average of 2 specimens.		60.1	39.9	31.5	8.4	7.3	0.7	0.4
" " dressed. " " " "		55.7	44.3	35.0	9.3	8.3	0.5	0.5
Hake, entrails removed..............	113	52.5	47.5	39.5	8.0	7.2	0.3	0.5
" " "	110	40.3	59.7	49.0	10.7	10.1	0.1	0.5
Haddock, entrails removed..........	16	51.4	48.6	39.0	9.6	8.9	0.1	0.6
" " "	21	51.6	48.4	39.7	8.7	7.8	0.1	0.8
" " "	229	48.0	52.0	42.9	9.1	8.3	0.2	0.6
" " "	259	52.9	47.1	38.5	8.6	7.9	0.2	0.6
" " Maximum of 4 specimens......		52.9	52.0	42.9	9.6	8.9	0.2	0.8
" " Minimum " "		48.0	47.1	38.5	8.6	7.8	0.1	0.6
" " Average "		51.0	49.0	40.0	9.0	8.2	0.1	0.5
Cod, head and entrails removed......	3	33.7	66.3	55.3	11.0	9.9	0.2	0.6
" " "	11	30.6	69.4	57.9	11.5	10.4	0.3	0.9
" " "	228	25.5	74.5	62.1	12.4	11.4	0.2	0.8
" whole...........................	206	56.5	43.5	35.1	8.4	7.7	0.1	0.6
" "	243	48.5	51.5	42.3	9.2	8.3	0.3	0.6

Table X.—Continued.

Names of Fish and Portions Analysed.	Laboratory Numbers of Specimens.	Refuse: Entrails, Bones, Skin, etc. per cent.	Edible Portion. Flesh. per cent.	Water. per cent.	Water-free Substance. (Nutrients.) per cent.	Albumin-oids (by difference). per cent.	Fats. per cent.	Mineral Matters. per cent.
Cod, dressed. Average of 3 specimens..........	99	29.9	70.1	58.5	11.6	10.6	0.2	0.8
" " " 2 " whole..........	81	52.5	47.5	38.7	8.8	8.0	0.2	0.6
Tom-cod, whole..........	1	59.9	40.1	32.7	7.4	6.8	0.2	0.4
Pollock, head and entrails removed	9	28.5	71.5	54.3	17.2	15.5	0.6	1.1
Halibut, posterior part of body, lean	211	23.1	76.9	60.9	16.0	13.4	1.7	0.9
" section of body, fatter than No. 1........		11.2	88.8	62.3	26.5	16.1	9.4	1.0
" sections from different parts of body......		18.7	81.3	62.6	18.7	15.8	2.2	0.7
" average of 3 specimens.....		17.7	82.3	61.9	20.4	15.1	4.4	0.9
Turbot, whole.....	49	47.7	52.3	37.3	15.0	6.8	7.5	0.7
Common flounder, entrails removed...........	2	57.0	43.0	35.8	7.2	6.3	0.3	0.6
" whole..	22	66.8	33.2	27.2	6.0	5.2	0.3	0.5
Winter flounder, whole........	253	56.2	43.8	37.0	6.8	6.1	0.2	0.5
Lamprey eel, whole........	236	45.8	54.2	38.5	15.7	8.1	7.2	0.4
Skate, left lobe of body........	247	51.0	49.0	40.2	8.8	7.5	0.7	0.6
SPENT FISH.								
Salmon, male, whole.....	35	43.8	56.2	42.3	13.9	10.8	2.5	0.6
" female, whole.....	36	43.5	56.5	44.2	12.3	10.0	1.6	0.7
" whole. Average of 2 specimens.......		43.6	56.4	43.3	13.1	10.4	2.1	0.6
" land-locked, male, whole........	40	48.4	51.6	40.2	11.4	8.7	2.1	0.6
" " female, whole........	41	46.2	53.8	42.6	11.2	9.5	1.0	0.7
" " whole. Average of 2 specimens........		47.3	52.7	41.4	11.3	9.1	1.6	0.6
ROE.								
Shad roe, from shad No. 245	246	0.0	100.0	71.2	28.8	23.4	3.8	1.6
PRESERVED FISH. **DRIED.** (Salt. per ct.)								
Desiccated cod, flesh desiccated and ground...... ...... (Salt 2.9)	79	0.0	97.1	15.2	81.9	74.6	1.9	5.4

Table X.—Concluded.

Names of Fish and Portions Analysed.	Salt. per cent.	Laboratory Numbers of Specimens.	Refuse: Entrails; Bones, Skin, etc. per cent.	Edible Portion. Flesh. per cent.	Edible Portion. Water. per cent.	Water-free Substance. (Nutrients). per cent.	Nutrients. Albumin-oids (by difference). per cent.	Fats. per cent.	Mineral Matters. per cent.
SALTED.									
Mackerel, "No. 1 mackerel."	7.1	42	33.3	66.7	28.1	31.5	14.7	15.1	1.7
SALTED AND DRIED.									
Salt cod, "Channel fish."	17.3	34	25.5	57.2	40.0	17.2	15.7	0.3	1.2
" "Boat fish."	17.2	37	24.3	58.5	40.5	18.0	16.4	0.4	1.2
" Average of 2 specimens	17.2		24.9	57.9	40.3	17.6	16.0	0.4	1.2
" "Boneless cod fish."	19.1	25	0.0	80.9	54.4	26.5	22.1	0.3	4.4
Desiccated cod, flesh desiccated and ground	6.6	80	0.0	93.4	11.7	81.7	71.6	4.9	5.2
SALTED, SMOKED AND DRIED.									
Smoked herring	0.5	33	44.4	49.1	19.2	29.9	20.2	8.8	0.9
" haddock	1.4	88	32.2	66.4	49.2	17.2	16.1	0.1	1.0
" halibut	12.0	28	8.0	80.0	47.0	33.0	16.7	14.4	1.9
" "	12.1	218	5.9	82.0	44.9	37.1	21.6	13.6	1.9
" " Average of 2 specimens	12.1		6.9	81.0	46.0	35.0	19.1	14.0	1.9
CANNED.									
Sardines	0.0	87	5.0	95.0	53.6	41.4	24.0	12.1	5.3
Salmon	0.4	29	11.7	87.9	58.2	29.7	18.8	9.8	1.1
"	2.2	96	0.0	97.8	62.2	35.6	19.7	14.6	1.3
"	0.4	241	0.0	99.6	57.6	42.0	19.2	21.5	1.3
" Average of 3 specimens	1.0		3.9	95.1	59.3	35.8	19.3	15.3	1.2
Mackerel	1.9	94	0.0	98.1	68.2	29.9	19.9	8.7	1.3
Salt mackerel, "No. 2 mackerel."	7.9	95	17.0	75.1	35.8	39.3	14.0	23.2	2.1
" " " Average of 2 specimens	8.7	219	22.4	68.9	33.8	35.1	13.7	19.3	2.1
" " "	8.3		19.7	72.0	34.8	37.2	13.8	21.3	2.1
Tunny, "Horse mackerel."	0.0	240	0.0	100.0	72.7	27.3	21.5	4.1	1.7
Smoked haddock	5.6	275	0.0	94.4	68.7	25.7	21.8	2.3	1.6

ON THE DETERMINATION OF THE ATOMIC WEIGHT
. OF OXYGEN.

By Edward W. Morley.

To determine the atomic weight of oxygen from the specific gravities of oxygen and hydrogen, it is necessary to know the ratio of the volumes in which they combine.   Gay Lussac found this ratio to be very nearly 2 : in computations of atomic weights it has usually been assumed that it is *exactly* 2.   This assumption was of course justified until we should have a better determination of the ratio.   In an interesting and important paper recently read before the Royal Society at London, Scott has made it very probable that the ratio is sensibly less than 2, and made it probable that it is less by some such quantity as .005.   The importance of the subject, shown by the fact that several chemists in this country and in Europe are reported to be engaged in a determination of the atomic weight of oxygen, leads me to offer some comments on the paper of Scott, from which I cannot separate some description of processes with which I am myself occupied.

In Scott's experiments, the mixture of oxygen and hydrogen was found to contain from a two hundredth to a three thousandth of its volume of nitrogen, perhaps mixed with carbon dioxide. By ingenious reasoning he deduces the conclusion that the ratio sought cannot be greater than 1.994.   Unless it be determined how much of this nitrogen came from the hydrogen and how much from the oxygen, it is possible only to determine a maximum and minimum value for this ratio.   The uncertainty will depend on the amount of impurity in the gases used in the experiment, and the uncertainty in the atomic weight of oxygen will be greater than the uncertainty in this ratio ; for unless Regnault was much more successful than Scott in preparing pure gases, the specific gravity of the gases according to his determinations will be as uncertain as the ratio of combining volumes, so that the uncertainty in the product of the two ratios will be doubled.

I have been occupied for some time with the redetermination of the atomic weight of oxygen.   One of the methods which I am preparing to use consists in weighing a sample of oxygen and one of hydrogen at a given pressure, determining the amount of

impurity in each gas, and determining the ratio of the combining volumes of the gases at the same pressure. Then a simple correction for the amount of impurity in each gas will give the ratio of specific gravities and combining volumes for the *pure* gases. The method involves the following operations :

1. A counterpoised globe *a*, a smaller globe *b*, a baromanometer, and a Sprengel pump are fused to a tube leading to an air pump. They also connect with a mercurial stopcock leading to a hydrogen generator. By the air pump, a high exhaustion is produced in the system. When the globes are exhausted and dried, dry hydrogen is admitted to the system ; this hydrogen will be at about the atmospheric pressure while passing through drying tubes, and will be expanded only on passing the mercurial stopcock, so that the drying tubes will not be rendered ineffective. The hydrogen will not pass through one globe to reach the other, but will pass simultaneously from the connecting tube to the two globes, so that both will contain samples of identical composition.

2. The globe *a* being at 0° C., the manometer will be read, and the globe fused off and weighed, while *b* will be still connected with the Sprengel pump and the manometer.

3. The globe *a* is connected with a second manometer and Sprengel pump, and with a third globe *c*, as before, also with an air pump and oxygen generator. The system is filled with oxygen, and the globe *a* is then fused off and weighed.

4. *b* and *c* now contain samples of oxygen and hydrogen identical with those weighed, capable of preservation for any length of time, and capable of transfer by the Sprengel pumps without the least admixture. A quantity of oxygen is taken from *c* and measured at the pressure at which the sample in *a* was measured for weighing ; two similar quantities of hydrogen are taken from *b*, these are mixed and exploded, the residue determined, exploded with oxygen or hydrogen as may be necessary, and the residual nitrogen determined.

5. Hydrogen is taken from *b*, but instead of passing at once to the eudiometer, it is passed through a tube containing heated copper oxide in a high vacuum. After passing into it, say, 200 cc. of hydrogen, the tube is cooled, and 200 cc. are passed in the cold and the tube exhausted till the whole gas passed into it has been carried out. By the manometer, the amount of gas passed in is measured; by the eudiometer, the gas remaining is measured;

so that the contraction by reduction of the copper oxide is known, and hence the difference between the percentage of impurity in the entering and outgoing gas is known. This hydrogen is mixed with a measured quantity of oxygen from *c*, exploded, and the residual nitrogen determined as before. For ease of explanation, suppose that in 4 the quantities involved were all known, and were as follows: hydrogen 200, containing 199 hydrogen and 1 nitrogen; oxygen 100, containing 99 oxygen and 1 nitrogen; after explosion, 2 nitrogen.

In the present operation the impurity in the hydrogen would be doubled, so that we should have: hydrogen 200, containing 198 hydrogen and 2 nitrogen; oxygen 100, containing 99 oxygen and 1 nitrogen; after explosion, 3 nitrogen.

It is obvious that the difference between the nitrogen found in 4 and in 5 is the nitrogen contained in the 200 cc. hydrogen which were consumed by passing over copper oxide.

6. In a similar way, oxygen from *c* is passed over heated copper so as to reduce 200 cc. to 100 cc., and this oxygen is exploded with hydrogen from *b*. We thus measure directly the nitrogen contained in the oxygen of *c*. The determinations of nitrogen from oxygen and from hydrogen check each other, for the sum must equal the nitrogen found in the first experiment.

We now have the data for correcting the weights of the oxygen and hydrogen weighed in *a* for the impurity contained in them, and also for correcting the results of the explosions, so as to get the ratio of combining volumes of *pure* hydrogen and oxygen. The accuracy to be expected depends on the accuracy of eudiometric measurements and of weighings. With the apparatus which I use for the experiments it is easy to reach an accuracy of one part in 25,000, and practicable to double this accuracy. As three determinations, each involving six measurements, are involved in the process, the average error to be expected in the process is one part in 10,000. Now, with a balance carrying 1200 grams in each pan, it is possible to weigh only about one gram of hydrogen. To determine this within less than half a milligram is very difficult. Even if the globe be sealed by fusion, so that weighings can be repeated for a long time, it would not be possible to depend on the weight of the hydrogen to one part in 10,000. In a second series of experiments, therefore, I intend to weigh a much larger volume of hydrogen or oxygen. In these experiments a globe as large as

can be made will be connected with a manometer and a mercurial stopcock, and exhausted.   A weighed generator, giving pure dry hydrogen, will be connected to it by a special joint, the sealed delivery tube of the generator be broken off, and gas passed into the globe.   Then the generator is sealed off and weighed, the globe is surrounded with melting ice, and the volume of the gas measured.   In this case the tubes connecting the globe with the manometer are filled with gas, not at 0°C., but at some other temperature.   The volume so filled, however, may be made small, and the resulting error may be made very small by measuring oxygen and hydrogen in the apparatus under identical circumstances.   If in this way it be possible to obtain five grams of hydrogen from an apparatus weighing not more than 1200 or 1500 grams, we can perhaps reduce the error in determining the ratio of the two specific gravities to a third or fifth of the error when a smaller volume is used.

With this large balloon it is necessary to store up a part of the gas first measured in it to be exploded with the gas measured second.   This involves its transfer to another vessel; but by exhausting this other vessel, admitting some of the gas, and exhausting again, the difference between the composition of the gas as measured and as stored in the other vessel may be made as small as is required.   The process for determining the residual impurity in each gas, and the ratio of combining volumes, is the same in this case as in the last.

It is hoped that individual results obtained by these methods will agree closely with each other and with the truth ; but the truth must be learned from the coincidence of the results of several methods.   Now it is well known that there are sources of constant error in the syntheses of water hitherto made by passing hydrogen over heated copper oxide ; I therefore expect to repeat this synthesis with the improvements suggested by the advance of our knowledge during the last forty years.   For instance, the apparent weight of the oxygen used in the synthesis is diminished by the amount of hydrogen absorbed by the reduced copper, and by the amount of oxygen mixed with the current of hydrogen.   The first error can be measured and a correction applied ; the second can be avoided.   It is also easy to devise apparatus which shall permit the weighing of the tube with copper oxide, and the tube for collecting water, deliberately, repeatedly, after any desired interval,

and with great accuracy. My experiments on the amount of moisture left in a gas after drying with sulphuric acid or phosphorus pentoxide were, in part, a study of the means of weighing similar apparatus much more accurately than is usual.

It is very likely that the constant errors just mentioned are very small, but the best assurance of this fact would be found in the agreement of results by this method with those by other methods, if such could be devised. Accordingly I shall make a synthesis of water from a weighed quantity of hydrogen. In one series of experiments, a generator with its drying tube will be sealed and weighed when freed from oxygen and nitrogen. It will then be connected by a leakage-proof joint with an apparatus where, after its fused point shall be broken off, a current of hydrogen will be mixed with dry oxygen in excess, and passed over heated platinum sponge and resulting water collected and weighed. The generator will again be sealed up and weighed.[1] The advantage of this process is mainly that it is *another* process, and that therefore the sources of constant and of accidental error in it will be different from those in the process with a weighed quantity of oxygen. It is well to note that there is no important advantage in determining the hydrogen directly. In the older process the water is determined by the difference of two weighings, the oxygen is determined by the difference of two other weighings, and the hydrogen by the difference of these differences. In the present process the hydrogen is determined by the difference of two weighings, the water by the difference of two, and the oxygen by the difference of the differences. Now, the weight of the hydrogen, however obtained, is a small number, and a slight absolute error is a large error relatively to this small number ; and this is equally true in both processes. The advantage of the new process is that the hydrogen is determined by two weighings instead of four, so that the error in its weight would in a large number of experiments be 30 per cent. less, if all the weighings were of something like similar amounts and capable of the same accuracy, which is a nearly correct supposition.

If the method just mentioned gives valuable results, I shall probably use another method which suggested itself before the last. It consists in weighing the hydrogen after first having it absorbed

[1] Keiser has made a similar synthesis by passing hydrogen over heated copper oxide. Is it possible in this way to burn completely a quantity of hydrogen?

by finely divided palladium, and sealing it in a flask. After breaking off the sealed point, the gas will be extracted by a Sprengel pump, aided by the use of heat, the gas will be mixed with a current of oxygen, and the resulting water collected and weighed.[1]

I have been devising the apparatus required for these determinations for more than three years. Owing to ill health, the only parts of the plan yet completed are the preliminary determination of the completeness of drying possible with sulphuric acid and phosphorus pentoxide. The vast amount of work required in devising and proving apparatus so complicated as that in hand is well known to those engaged in similar labors. This is now approaching completion; I hope for useful results at no very distant day.

CLEVELAND, OHIO, *November* 29, 1887.

INVESTIGATIONS ON THE OXIDATION OF SEWAGE.

BY J. H. LONG.

Something over a year ago I began a series of experiments for the Illinois State Board of Health, intended to show the rate of oxidation or destruction of sewage in a canal flowing west from the city of Chicago, and discharging finally into the Illinois river.

The peculiar situation of Chicago and its system of drainage dependent on this make such tests unusually interesting, and I wish, in the following, to present some of the results obtained in the work.

Only a few miles south and west of the city is found the low watershed separating the basin of Lake Michigan from that of the Mississippi. On the Chicago side of this " divide " is the Chicago river, mostly within the city limits, which serves as a harbor for shipping, and likewise as a receptacle for the greater part of the sewage from a population of about 800,000.

Many years ago the Illinois and Michigan Canal was constructed, connecting Lake Michigan through the river with the

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[1] The use of palladium for the synthesis of water independently suggested itself to Keiser. I described my method in conversation in October, 1884.

Illinois river at a point about 48 miles southwest of the city. This canal is supplied with water by pumps located at Bridgeport, within the city limits, five miles from the lake, which at present lift about 50,000 cubic feet per minute and discharge it toward the west.

The canal, then, at its eastern end, is fed by dilute sewage, and it is the changes in this that I have to explain.

This dilute sewage is made up chiefly of three elements:

1. Of the water of Lake Michigan. This water contains in parts per million 136 parts of total solids, and furnishes of free ammonia from 0 to .01 part per million, and of albuminoid ammonia .070 part per million. In oxidation by the Kubel process about one part per million of oxygen is required.

2. Of about 70,000,000 gallons per day of sewage proper. We have no accurate data showing the average composition of this as it leaves the sewers, but samples taken near the mouths of some of these showed large amounts of free ammonia, indicating an advanced stage of decomposition.

3. Of about 7,000,000 gallons daily of sewage from the large stockyards south of the city. The character of this has been investigated. In samples analysed last autumn I found the solid matter to amount to about 9200 parts per million, with between 3000 and 4000 parts of organic matter. Samples were taken every hour through the twenty-four, mixed and analysed, after dilution with pure water. In this way I found for one day, October 29th, in parts per million:

Free ammonia, ...	42
Albuminoid ammonia, ...	6.4
Oxygen consumed, ...	208

The results obtained on other days averaged about the same.

Collection and Analysis of Samples.

The waters were taken in gallon jugs on the same day at the several stations, and sent to me by express. They were examined as soon as possible after their receipt.

After necessary dilution with pure water I determined free and albuminoid ammonia, taking precautions to make these experiments as accurate and uniform as practicable. I also found the consumption of oxygen by the Kubel process. Full details of the

several methods, as followed, were given in my reports to the State Board of Health last winter, which, however, are not yet published.

The Water at Bridgeport.

Ten analyses were made of the water just as it reached the pumps. The first tests were made on water taken on June 26th, 1886, and the last on water taken on August 28th, with results as follows:

	In 1,000,000 Parts.		
	Free Ammonia.	Alb. Ammonia.	Oxygen consumed.
June 26	2.6	.64	12.0
July 3	2.7	.52	6.8
10	4.2	.62	16.8
17	25.0	1.50	22.4
24	5.5	.37	12.6
31	23.0	1.76	23.2
Aug. 7	26.0	1.50	16.8
14	29.0	1.64	32.0
21	27.2	1.50	28.0
28	29.2	1.90	35.2
Mean	17.44	1.195	20.58

The smaller amounts of contamination in the first tests can be accounted for by the fact of a high lake level, in consequence of which the sewage outflow from the stockyards' sewer and other sewers was at times much retarded and a comparatively clean water reached the pumps from the lake.

The Water at Lockport.

After leaving the pumps the water flows along the level to Lockport, 29 miles below, requiring about a day for its passage. The canal water receives no additions between the two places, that is, it is not diluted by any other stream or feeder. The rainfall during the summer of 1886 was unusually small, in fact, the lowest in 15 years. Dilution from this source can be left quite out of consideration, and owing to the frequent passage of propellers and other boats no very great change in the character of the water by sedimentation could take place.

The tests gave:

				In 1,000,000 Parts.		
				Free Ammonia.	Alb. Ammonia.	Oxygen consumed.
June 26	.	.	.	2.8	.56	11.36
July 3	.	.	.	2.4	.42	7.2
10	.	.	.	...	...	...
17	.	.	.	10.2	.72	12.8
24	.	.	.	9.2	.47	14.8
31	.	.	.	11.0	.72	10.7
Aug. 7	.	.	.	12.0	.48	9.6
14	.	.	.	15.2	.88	9.76
21	.	.	.	15.0	.84	10.8
28	.	.	.	13.0	.88	12.4
Sept. 4	.	.	.	11.5	.72	13.6
Mean	.	.	.	10.23	.669	11.30

The Water at Joliet.

After passing Lockport the water descends to Joliet through four locks, and falls over a dam seven feet in height, to point of collection. There is a fall of 58.2 feet in a distance of four miles, and no dilution takes place on the way.

The tests gave results as follows:

				In 1,000,000 Parts.		
				Free Ammonia.	Alb. Ammonia.	Oxygen consumed.
June 26	.	.	.	1.7	.46	7.36
July 3	.	.	.	1.8	.46	9.76
10	.	.	.	2.4	.56	9.20
17	.	.	.	13.0	.44	14.50
24	.	.	.	...	...	...
31	.	.	.	9.2	.44	5.68
Aug. 7	.	.	.	7.5	.42	5.84
14	.	.	.	9.8	.46	5.76
21	.	.	.	9.0	.112	.520
28	.	.	.	8.0	.32	6.80
Mean	.	.	.	6.93	.408	7.79

Although there are certain irregularities in the above table which cannot now be explained, a general decrease of organic matter is plainly shown; and it will also be noticed that the percentage of

loss per mile is much greater between Joliet and Lockport than between the latter and Bridgeport. This is undoubtedly due to the more perfect aeration of the water secured by the passage through the locks and over the dam.

The loss per mile is this, expressed in terms of amount at upper station:

	Free Am.	Alb. Am.	Oxygen used.
Bridgeport to Lockport,	1.44 per ct.	1.52 per ct.	1.55 per ct.
Lockport to Joliet,	8.06 per ct.	9.75 per ct.	7.76 per ct.

Thus the loss of free ammonia per mile between Bridgeport and Lockport is 1.44 per cent. of the amount at Bridgeport, while the loss between Lockport and Joliet is 8.06 per cent. of the amount at Lockport.

Through a good part of its course the canal flows parallel to the Des Plaines river, which, 48 miles below Bridgeport, unites with the Kankakee to form the Illinois, into which also a large portion of the canal water is diverted.

The next tests were made at Ottawa, 48 miles below Joliet and 73 feet lower. The Fox river joins the Illinois at this point, so that the canal water becomes very much diluted. From surveys and measurements made recently it has been estimated by Mr. L. E. Cooley, of the Chicago Drainage and Water Supply Commission, that at the period under investigation—the summer of 1886—43 per cent. of the water at this point came from the canal, and the rest from the streams named.

The chemical tests gave:

	In 1,000,000 Parts		
	Free Ammonia.	Alb. Ammonia.	Oxygen consumed.
June 26	.50	.23	7.05
July 3	.104	.21	.576
10	.22	.164	4.96
17	.56	.252	6.54
24	...	...	...
31	.49	.250	6.00
Aug. 7	.52	.32	6.40
14	.30	.144	4.80
21	...	...	...
28	.36	.33	3.12
Mean	.382	.237	5.57

These figures show a remarkable decrease in the free ammonia, the loss amounting to 94.5 per cent. of the quantity at Joliet. This is partly accounted for by the large dilution, as 57 per cent. of the water here comes from sources other than the canal, as explained ; but, unfortunately, it is not possible to express numerically the effect of this dilution, as we do not know the exact composition of diluting waters.

At first sight it would appear that, taking into consideration the amount of dilution, instead of there being a loss of albuminoid ammonia and oxygen consumed there is a gain in this flow of 48 miles. This apparent anomaly can be explained, I think, without great difficulty.

The streams feeding the Illinois flow through a rich soil and partly swampy regions, where relatively large quantities of organic matter are taken up. The Sangamon river in this State is in some respects analogous to the Kankakee. I analysed a sample of its water taken at Decatur in the summer of 1885, and found it very highly contaminated with vegetable matter, partly suspended and partly in solution. The organic matter dissolved amounted to about 40 parts per 1,000,000, and other tests gave in parts per 1,000,000 :

Free ammonia 013
Alb. ammonia 170

I have no doubt that the river water at Ottawa, free from sewage, would show as large an amount of nitrogenous matter as these figures indicate.

It must also be remembered that the sewage of several towns enters the river above Ottawa. Joliet, which is sewered pretty completely, has a population of 15,000, while the other sewered places may have 5000 more. It is fair, then, to believe that a moderate change in the amount of organic matter has occurred between the two stations. The probability of such change is shown by the determinations made at Peoria, 78 miles below Ottawa, but at a lower level of only 15.5 feet.

There are no tributaries of any consequence between these cities. The proportion of canal water is decreased only from 43 per cent. to 39 per cent., while sewage from several important towns is taken up.

It may also be added that the total flow at Peoria amounted to

about 125,000 cubic feet per minute at the time of the tests, while about 22 days were required for the descent from Ottawa.

The tests gave:

				In 1,000,000 Parts.		
				Free Ammonia.	Alb. Ammonia.	Oxygen consumed.
June 26	.	.	.	.036	.150	5.04
July 3	.	.	.	...	...	...
10	.	.	.	.084	.150	5.04
17	.	.	.	...	...	...
24	.	.	.	...	...	...
31	.	.	.	.0048	.196	4.64
Aug. 7	.	.	.	.0072	.210	6.80
14	.	.	.	.042	.190	4.72
21	.	.	.	.066	.212	4.88
28	.	.	.	.009	.206	2.80
Mean	.	.	.	.0355	.1877	4.85

Unfortunately, there are three breaks in this table, due to the neglect of the persons expected to forward the water. The tests carried out showed, as at Ottawa, a marked loss of free ammonia, which must be explained chiefly by oxidation. There is likewise a perceptible diminution in the amount of oxygen consumed and in the albuminoid ammonia, even after the dilution is taken into consideration.

It is plain that in this long stretch of 78 miles with a fall of only 15 feet the water must be in many places practically stagnant, and we know that under such circumstances oxidation of organic matter is necessarily slow. The conversion of ammonia into nitrates is apparently much more rapid. It is possibly true that the residual organic matter represented by the oxygen consumption and albuminoid ammonia is of a relatively stable type, capable of resisting complete change for a long period, but which may be broken up with comparative ease by the reagents of the laboratory processes. Many of the vegetable matters finding their way into these waters are of that nature, as numerous experiments have shown.

It must also be borne in mind, as mentioned above, that a certain amount of sewage is discharged into this portion of the river, and taking all these points into consideration, it is fair to conclude that destruction of organic matter is going on here at a moderate rate, but less rapidly than above.

It would be interesting to know the condition of affairs in the stream between Peoria and its junction with the Mississippi, a distance of some 200 miles. An investigation of this nature is contemplated for the near future.

The above tests show in a fair and unmistakable way the general fact of the gradual purification of a highly contaminated water by what may be broadly termed oxidation. In the upper part of the course sedimentation cannot be called into account for much of this change, as the water undergoes frequent agitation by passing boats. In the lower part of the course this disturbance is less frequent, but at the same time the matter which could be lost by sedimentation is less abundant.

I am therefore led to attach considerable importance to these investigations, as showing pretty fully the rate at which a city's sewage is destroyed under certain conditions of temperature, dilution, and velocity of flow. In most similar investigations these important data are given imperfectly or not at all, so that to draw a legitimate conclusion is almost impossible.

Oxidation in Winter.

It is generally admitted that destruction of sewage is less rapid in winter than in summer, although direct chemical experiments bearing on that point are very few.

During last winter the above investigations were continued so as to show as nearly as possible just what the effect of the cold really is. The waters were taken at the same places by the same observers and examined in the same way. The results of these examinations are given in the following table—the results expressed in parts per 1,000,000 :

From.	When taken.	Free Ammonia.	Albuminoid Ammonia.	Oxygen consumed.
Bridgeport, . . .	Dec. 18,	17.60	4.80	28.8
	Jan. 18,	6.60	3.50	16.0
	29,	5.90	3.80	22.4
	Feb. 3,	10.60	3.70	32.8
Lockport, . . .	Dec. 6,	3.70	.56	17.6
	Jan. 3,	9.20	3.90	21.6
Joliet, ...	Dec. 7,	11.00	.60	16.8
	13,	13.00	1.80	19.2
	20,	13.20	3.30	21.6
	27,	18.40	4.90	24.8

3

From.	When taken.		Free Ammonia.	Albuminoid Ammonia.	Oxygen consumed.
Joliet, ...	Jan.	1,	11.60	3.72	19.6
		8,	8.40	4.20	18.4
		15,	5.40	3.00	10.0
		22,	3.24	1.76	14.4
		29,	3.20	1.54	10.0
	Feb.	4,	3.80	2.22	19.2
Ottawa, ...	Dec.	9,	1.52	.54	10.4
		13,	5.74	2.60	15.2
		22,	6.80	1.20	11.2
		28,	.96	2.92	*60.0
	Jan.	4,	8.20	2.70	10.8
		8,	2.20	2.80	*44.0
		22,	2.60	.30	6.8
		29,	.36	.32	†11.2
	Feb.	5,	3.70	.38	9.2
		12,	3.20	.46	10.8
Peoria, ...	Jan.	15,	1.26	.25	4.4
		22,	3.60	.68	7.36
		29,	.52	.36	7.60
	Feb.	2,	.90	.36	8.80
		7,	.72	.34	7.90

In the above table there are many perplexing irregularities, some of which can be explained, while for others the data are lacking.

On the 7th of December, owing to an accident, pumping was stopped at Bridgeport, and did not begin again until December 27th. During this time the flow under the ice through the canal amounted to about 15,000 cubic feet per minute by gravity, while the flow in the small rivers below was likewise lessened. After December 27th the pumps forced about 50,000 cubic feet per minute through the winter.

In January there is shown a decrease in the free ammonia with an increased amount of albuminoid ammonia and oxygen consumed at Bridgeport and Joliet, as compared with the summer rate, while at Ottawa and Peoria all these factors are increased. After the close of navigation sedimentation plays an important part in

* Very unusual color and odor.

† This sample was taken on January 29, but not forwarded until a week later.

the still water. For this reason purification appears more rapid than is actually the case.

Near the source of contamination we can understand that free ammonia is not so quickly formed, because of the low temperature ; and for the same reason, when once formed, it is not so readily oxidised at points further down in the stream.

The effect of the stoppage of the pumps is shown in the albuminoid ammonia as late as January 8th at Ottawa. After this date, between Ottawa and Peoria there seems to be no change in the organic nitrogenous matter, the amount at the latter place being about twice as great as during the summer.

The waters collected at Peoria during the summer were without odor, while through the winter it was frequently quite marked. It is said to be very noticeable at holes broken in the ice, and if the filth left above by deposition reached here it would be much worse.

This state of the water can be partly accounted for by the diminished flow from some of the streams feeding the Illinois, but the chief factor is undoubtedly the low temperature. A coating of ice excludes the air, and thus prevents direct oxidation when this is possible. A more important result of lower temperature is found in the diminished activity of bacterial ferments. These are probably the chief agents in the decomposition of organic filth, and their efficiency is greatest at moderate temperatures.

The above experiments, while not as complete as could be desired, show several important points. Even under the unfavorable conditions in the canal and river, it is seen that sewage is pretty rapidly decomposed in summer. With a greater velocity of the flowing water this change would undoubtedly be much more complete.

The slow rate of winter change is clearly shown. These results suggest another very interesting inquiry, viz: At what rate is *rapidly moving* sewage oxidised in winter ? An answer to this, with statement of all conditions, would have a great practical value.

NOTES OF WORK FROM THE CHEMICAL LABORA-
TORY OF THE UNIVERSITY OF VIRGINIA.
No. XVI.

Communicated by F. P. DUNNINGTON.

134.—ON TITANIC OXIDE IN SOILS.

By J. F. McCALEB.

Through the analysis of what proved to be a fulgerite, which was described by me before the Chemical Section of the A. A. A. S. at its meeting of 1885,[1] titanic oxide was found to exist in certain soils of Albemarle Co., Va.

Attention has also been called, in a communication from this laboratory,[2] to the wide distribution of titanic oxide as menaccanite, and also as imparting color to the blue quartz which occurs so abundantly throughout the Piedmont region of Virginia. It was therefore proposed to Mr. McCaleb to examine for titanic acid the soils of this vicinity and some others of which specimens were in hand.

The method pursued was that brought forward by A. Weller.[3] The powdered soil was fused with sodium acid sulphate, exhausted with cold water, the filtrate brought to a measured volume and hydrogen dioxide added; the yellow color thus produced was compared with that similarly obtained from a standard solution of titanic oxide. With each specimen the undissolved residue was re-fused with sodium acid sulphate until either very little or no titanium was found in the filtrate.

Samples of soil were taken from nine points, situated approximately in three lines, all parallel to the Southwest Mountains, which are about twenty miles southeast of the Blue Ridge and parallel to it.

Nos. (1), (2) and (3) from the slope of the Southwest Mountains and about one mile apart, all deep red soil; (2) being from the location of the fulgerite.

[1] Proc. **A. A. A. S. 34**, 132.   [2] Chemical News **50**, 207.
[3] Berichte der deutsch. chem. Gesell. **15**, 2592.

Nos. (4), (5) and (6) from corresponding points near the bottom of the mountain and in a line one-half mile distant. (4), alluvial in the bottom ; (5), white sandy soil beyond the bottom ; (6), red diorite soil beyond the bottom.

Nos. (7), (8) and (9) from corresponding points on rising ground, in a line two miles further to the northwest. (7), white micaceous soil, on higher land—from a micaceous schist ; (8), red diorite soil, near the laboratory of the University ; (9), white sandy soil, on slope of Observatory Mountain.

To these were added : (10), red soil, from Red Hill, situated about ten miles southwest of the University and geologically in the same belt of country ; (11), alluvial soil from swamp on Rappahannock River, Stafford Co., Va.; (12), "black canebrake soil," near Uniontown, Perry Co., Alabama ; (13), "alkaline soil," Truckee Valley, Nevada.

After Mr. McCaleb had examined the foregoing specimens I found opportunity to collect the following, in which also I estimated the titanic oxide : (14), red soil, from the Miller School farm, twelve miles west of the University ; (15), deep red soil, near large deposit of titanic oxide, six miles east of Lowesville, thirty-five miles southwest of the University ; (16), "limestone soil " lying at the foot of a hill of gneiss rock, Worthington's Valley, twenty miles northwest of Baltimore, Md.

The percent. of titanic oxide found in each of these respectively is as follows:

(1), 2.73	(5), .33	(9), .77	(13), .57
(2), 5.42	(6), 2.73	(10), 1.86	(14), 1.51
(3), 1.45	(7), 1.14	(11), .88	(15), 1.87
(4), 1.73	(8), 2.86	(12), .78	(16), 1.17

No doubt the fact that titanic oxide has not been observed to occur so generally distributed in soils is due to the unsatisfactory nature of the tests by which it heretofore was to be detected, when present in small amounts; but now that this test of A. Weller so simplifies the operation, it is hoped that soils in many other portions of the country will be so examined.

135.—ANALYSIS OF TSCHEFFKINITE FROM NELSON COUNTY, VIRGINIA.

By R. C. Price.

This mineral was discovered on Hat Creek, about 4 miles east of Massie's Mills, Nelson Co., Va. As far as I can ascertain, but a single lump weighing over twenty pounds has been found, and this lying loose upon the ground, where it was improbable that it had been transported any distance. There is much rutile in this vicinity, and in the same belt of country, within 15 miles, allanite has been found at two points in considerable amounts, as was described in previous communications[1] from this laboratory.

The piece examined appears to have been broken from a vein-like deposit 5 cm. thick, with a brown crust on either side where contaminated with the adjacent rock, but showing little evidence of weathering on other surfaces. It is amorphous and dull black, on a surface of fracture, with a few thin seams presenting a vitreous lustre, which latter were excluded from the portion analysed. Streak, grey; hardness, nearly 6; specific gravity, 4.4; fuses before the blowpipe at 3, with much intumescence, to a black glass. Is not magnetic before or after heating. Decomposed slowly by hydrochloric acid with separation of silica.

With borax it affords a clear yellow-brown glass, and with salt of phosphorus, a milky bead with pale brownish pink color.

For analysis it was decomposed by fusion with sodium acid sulphate, digested in cold water, and the silica filtered off and refused. The titanium was then precipitated by boiling, weighed, refused and redetermined in the solution by the calorimetric method with hydrogen dioxide, and the small amount of iron in this precipitate was estimated after reduction by sulphurous acid, the sum of these closely agreeing with the previous weight of the crude titanic acid precipitate.

For the determination of ferrous oxide the mineral was decomposed by heating in a sealed tube with hydrochloric acid and then titrated with permanganate. The separation of cerium, lanthanum and didymium was obtained by the methods of Winkler and Gibbs. Most of the determinations were made in duplicate, giving the following result:

[1] Chemical News **30**, 141; This Journal **7**, 177.

		Oxygen Ratio.	
SiO_2	23.28	776	776
TiO_2	21.16	579 } 617	
ZrO_2	2.29	38	
Ce_2O_3	11.89	108	
Di_2O_3	15.38	136	
La_2O_3	4.96	46 } 396	
Fe_2O_3	5.63	106	
FeO	5.56	77	
BeO	2.15	86	
CaO	5.48	97 } 276	
MgO	.64	16	
Na_2O	.32	5	
H_2O	1.90	106	

<div align="center">100.64</div>

When considering the cerium earths as protoxides, tscheffkinite was classified by Dana[1] as a subsilicate with titanic oxide basic; the oxygen ratio for

$$SiO_2 : TiO_2 : R_2O_3 : RO = 5 : 4 : 2 : 4.$$
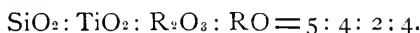
With these earths sesquioxide, the above must be rejected; and in order to consider the published analyses of tscheffkinite (1) and (4),[1] I have assumed the cerium earths to exist in the same proportions as have been found in the present specimen, which affords oxygen ratio for them as follows:

	SiO_2.	TiO_2.	R_2O_3.	RO.
(1), Ilmen,	77	55	44	25
(4), Coromandel,	77	64	44	24
Nelson County,	78	62	40	28

From the inspection of these figures it appears highly probable that the titanic oxide should be regarded as replacing silica. The composition of the Nelson County mineral approximates to

$$2(Ca, Be, Fe, Mg)O . (Ce, Di, La, Fe)_2O_3 . 5(Si, Ti)O_2,[2]$$
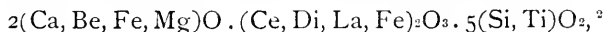
and the formula of each of the above will fairly correspond to a bisilicate of the amphibole group, with silicon replaced by titanium.

[1] System of Mineralogy, 5th ed., p. 388.
[2] Since writing the above I find in Tafel-Uebersicht der Mineralien, Groth assigns a similar formula to both tscheffkinite and keilhauite.

136.—OXIDATION OF SOLUTIONS OF SULPHUROUS ACID AND SULPHITES.

By I. A. Bachman.

In a former communication from this laboratory, No. 115,[1] it was shown by Mr. Reese that solutions of sulphites are more rapidly oxidised on exposure than is sulphurous acid.

In continuation of this subject, it was proposed to Mr. Bachman to examine the relative rates of oxidation of the sulphites of the alkalies.

Five solutions were prepared, one litre of each containing 10 grams of sulphurous oxide, and by addition of the requisite amounts of the solutions of the alkaline hydrates there were obtained the following: A, sodium sulphite; B, potassium sulphite; C, ammonium sulphite; D, ammonium acid sulphite; E, sulphurous acid.

One litre of each of these was put into a half-gallon green glass acid bottle. These were kept in a cupboard, but exposed to daylight, the stoppers left out, and to promote oxidation, twice daily (except Sundays) the stoppers were inserted and the contents vigorously shaken.

After making all these solutions, on the same day, 5 cc. of each was treated with hydrogen dioxide and ammonia, and the sulphuric acid then precipitated as barium sulphate; again, 5 cc. of each was titrated with iodine solution, and all subsequent estimations of sulphurous oxide also were made by Bunsen's method. Samples were drawn at stated intervals and estimations made, with the results which are tabulated below.

Grams of SO_2 found in 1000 cc. of solution:

	Na_2SO_3. A.	K_2SO_3. B.	$(NH_4)_2SO_3$. C.	NH_5SO_3. D.	H_2SO_3. E.
After 2 hours, estimated by $BaSO_4$, ...	9.75	9.80	9.76	9.40	...
After 3–4 hours, estimated by I, . . .	9.14	8.68	9.20	9.51	8.03
After 1 day, estimated by I, ...	8.05	7.86	7.88	9.25	8.28
After 1 week, estimated by I, ...	4.14	3.26	4.46	8.05	5.54
After 2 weeks, estimated by I, ...	.77	.37	1.31	6.71	3.25

[1] Chemical News **50,** 219.

	Na_2SO_3. A.	K_2SO_3. B.	$(NH_4)_2SO_3$. C.	NH_5SO_3. D.	H_2SO_3. E.
After 3 weeks, estimated by I, ...	tr.	tr.	tr.	5.11	1.88
After 3 weeks, SO_2 oxidised, ...	all.	all.	all.	2.73	.67
After 3 weeks, SO_2 volatilised, ...	none.	none.	none.	1.96	7.25

From which we may draw the following conclusions :

First. There is very little difference in the rate of oxidation of the sulphites of sodium, potassium, and ammonium.

Second. There is a marked advantage in employing an acid sulphite where it may be substituted for a solution of a sulphite or of sulphurous acid and is to be kept as a reagent or dispensed as a medicine.

It may be added that this presents an illustration of the fact that the solution of an acid salt is not a mere mixture of neutral salt with free acid in solution.

137.—ANALYSIS OF VARVACITE FROM WYTHE CO., VIRGINIA.

BY P. H. WALKER.

This mineral was received from Mr. J. C. Raper, being found on his land near the lead and zinc mines of Austinville, Wythe County, Va.

It occurs imbedded in psilomelane and ferruginous clay, is in radiating fine fibrous crystals, the layers being 10 to 20 mm. in thickness. Color and streak brownish black. Hardness 1.5, soiling the fingers. Fuses at about 4, imparting streaks of green to the flame. Specific gravity 3.27. Analysis gave :

		Atomic Ratios.	
MnO_2	68.86	791	8
MnO	7.51	105	1
BaO	14.42	94	1
H_2O	5.08	282	3
SiO_2	1.98		
Fe_2O_3 and Al_2O_3	2.23		
	100.08		

It is of interest to note the large amount of barium in a specimen so well crystallised. The composition, excepting the barium, accords with that of varvacite, which is regarded by Dana[1] as an impure pyroluscite or manganite. The analysis also suggests lepidophacite,[2] for which Jenkins assigns the formula $CuMn_6O_{12} + 9H_2O$. In this view the above figures correspond to $BaMn_9O_{18} + 3H_2O$.

138.—ATTEMPT TO FORM ARSENIC NITRIDE.

By I. A. Bachman.

In view of the similarities of arsenious and boracic oxide, of the stability of boron nitride, and also of the recent production of arsenic phosphide,[3] the production of arsenic nitride was undertaken.

In the following account of the various experiments no record is made of the trials which proved unsatisfactory either by reason of too little heat or of explosions, of which there were many, some giving a loud report. To secure safety in opening the sealed tubes, care was taken to draw off one end to a fine bore, and when this was pinched off the pressure was relieved gradually.

Dry ammonia was passed over gently heated arsenious oxide; this resulted in condensation, in the cooler portion of the tube, of arsenic, arsenious oxide, and water only.

Into a combustion tube was introduced successively a mixture of ammonium sulphate and magnesia, asbestos plug, arsenious oxide, the air displaced by dry hydrogen, and the tube sealed. This was heated within an iron tube for one hour to about 300° C. On opening it (by cracking it lengthwise with a small flame) there was found, in separate deposits, arsenic, arsenious oxide, and at the least heated end of the tube arsenious sulphide.

To avoid the formation of a sulphide a tube was then charged with ammonium carbonate, lime, and arsenious oxide, separated by asbestos, the air displaced by hydrogen, and the tube sealed. This was heated for two hours to, probably, 350° C. at its hottest portion. After cooling, the tube was opened; it contained gases under great pressure and a heavy deposit of arsenic, most of the arsenious

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[1] System of Mineralogy, 5th ed., pp. 166, 182.
[2] System of Mineralogy, 5th ed., Appendix III, p. 130.
[3] Berichte der deutsch. chem. Gesell. **6**, 216.

oxide having been reduced, but no indication of any combination with nitrogen was presented.

Another series of experiments was then made, aiming to effect combination between the elements of cyanogen and arsenious oxide. A tube was charged with silver cyanide, asbestos, lime, asbestos, arsenious oxide, leaving half of the tube empty, and then sealed. It was heated rather hotter than before, probably 400° C., for two hours, and after cooling was opened. The lime had been largely converted to carbonate. The portion of the tube in which the arsenious oxide had been put was heated hottest and was found empty; above it was deposited in order arsenic, " brownish arsenious oxide," white arsenious oxide, and at the far end of the tube a moderate amount of a chocolate-brown deposit. The latter was found to afford ammonia on being heated in a tube with soda-lime, and to consist essentially of arsenious oxide.

It was then attempted to separate the portion containing nitrogen by gentle heat in a current of dry nitrogen, but this merely resulted in volatilising the whole, with a condensation of only arsenious oxide and arsenic.

In other tubes similarly charged it was noted that if any moisture was left in the tube ammonia was formed, and none of this brown substance.

It was then found best to charge the tube with silver cyanide, asbestos and arsenious oxide, heat just a little short of volatilising the arsenic, and then, on opening the tube, the arsenious oxide was altered to a loosely coherent chocolate-brown (in some cases almost black) substance, with the following properties: Heated in a closed tube, at first arsenious oxide volatilises, the mass becoming darker, melting, and then subliming to form a ring of arsenic, together with a thin brown deposit and arsenious oxide, insoluble in alcohol, ether, chloroform, carbon disulphide. Water dissolves it more rapidly than dilute acids do; dilute hydrochloric acid attacks it slowly; strong boiling hydrochloric acid or nitric acid turns it lighter in color and gradually dissolves it. Strong hot sulphuric acid completely dissolves it to form a yellow liquid, which on further heating loses this color; caustic soda solution does not completely dissolve it on boiling; fused caustic soda does dissolve it with decomposition. By aid of the microscope it appeared that the brown substance was a coating over the arsenious oxide crystals.

Ignited by Ruffle's method, it afforded of nitrogen, by titration,
1.8 per cent. ; by nesslerising, 2.1 per cent.   An estimation of the
arsenic gave 76.61 per cent. ; no satisfactory determination of the
oxygen was made.   It was thought possible that some paracy-
anogen might be present, but this brown material does not soil the
fingers at all, and on combustion in a current of air affords only
a minute amount of carbon dioxide.   It appears, therefore, highly
probable that this body contains arsenic nitride, but no method of
removing the excess of arsenious oxide was discovered, and the
approach of the close of the session prevented a continuation of
the work.

139.—ANALYSIS OF "GENTHITE" FROM NORTH CAROLINA.

By P. H. WALKER.

An analysis of this mineral, from Webster, Jackson Co., N. C.,
was made in this laboratory some time ago, and published ;[1] but
since but very little of the material was then available and the
analysis not very satisfactory, it was of interest to repeat the work.
Through the kindness of Dr. Memminger, of Charleston, some of
this mineral was recently obtained.   It occurs in layers of 1 to 3
mm. in thickness, penetrating a ferruginous sandstone.   It is
amorphous, of a light apple-green color, translucent, greasy;
hardness, 2.5 ; specific gravity, 2.53.   After drying over sulphuric
acid, it gave on analysis :

		Atomic Ratio.	
SiO_2	55.38	923	3.
NiO	17.84	238	} 2.04
MgO	15.62	390	
H_2O at 100° C.	5.18	288	.94
" above "	5.59	310	1.01
Fe_2O_3	.56		
	100.17		

From which it appears that this mineral has the formula
$$[\tfrac{1}{3}H_2O + \tfrac{2}{3}(Mg, Ni)O] SiO_2 + \tfrac{1}{3}H_2O,$$
and may be regarded as a nickel-sepiolite.
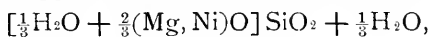
[1] Chemical News **26**, 654.

140.—ANALYSIS OF A NICKELIFEROUS TALC.

BY I. A. BACHMAN.

Together with the foregoing specimen there was received from the same locality a ball of material which had apparently been worked to its shape by the hand when moistened with water. It is composed of minute micaceous scales, of pale yellowish green color, with a few brown particles and grains of silica scattered through it. It is readily crushed to an unctuous powder. Specific gravity 2.31. After removal of the sand and drying over sulphuric acid, analysis gave:

		Atomic Ratio.	
SiO_2	53.91	898	5.16
NiO	15.91	212 }	
MgO	19.39	485 }	4.
Fe_2O_3	1.46	9	
Al_2O_3	2.65	25	
H_2O at 100° C.	.80	44 }	
" above "	5.50	306 }	2.01
	99.62		

These figures fairly agree with the formula

$$[\tfrac{1}{5}H_2O + \tfrac{4}{5}(Mg, Ni)O] SiO_2 + \tfrac{1}{5}H_2O,$$
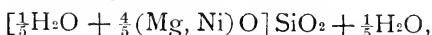
which is that given for hydrated talc. It is to be noted that nickel has previously been found in talc, but in small amounts; see analyses (11), (12), (27) and (35), quoted by Dana.[1]

141.—ON A FREEZING MIXTURE.

BY I. A. BACHMAN.

The most commonly used mixture for obtaining, on a small scale, temperatures between —20° and —40° C. is that of snow and commercial hydrochloric acid. Since diluted sulphuric or nitric acid can be similarly used, it was thereby suggested that we might utilise for this purpose the mixture of equal volumes of strong nitric and sulphuric acid which had been employed in a Grove battery and for which we had little further use, frequently throwing away much of it. When first made, the

[1] System of Mineralogy, 5th ed., p. 453.

mixture of acids has a specific gravity of about 1.63, and when spent, about 1.57.

Mr. Bachman undertook to ascertain in what mixture this spent acid can be best employed for obtaining a freezing mixture. The temperature of the atmosphere in which the trials were made ranged from —2° to +2° C., and in each instance the acid was brought to the temperature of the air before mixing with the snow. Diluting the acid with differing amounts of water and mixing these with snow, it was found that the undiluted acid and that diluted with one-tenth of the volume of water gave equal diminution of temperature; any large addition of water lessened the cooling effect.

The following results were obtained:

100 cc. acid and 225 grams snow gave fall of 31° C.
100 "   "   "   285   "   "   "   "   32° C.
100 "   "   "   340   "   "   "   "   30° C.
100 " HCl "   200   "   "   "   "   30° C.

As there was so little difference in the result when the snow was used within so wide limits, it was found most satisfactory to mix the snow with the acid until it attains the consistency of a thin mush, thus dispensing with all weighing. It is to be noted, as is explained by the above, that when the snow is wet, the temperature to be obtained with it is almost as low as when it is dry, which is far from being the case when hydrochloric acid is used.

It will also be seen from the above figures, that when working at a temperature near zero, the " spent acids " answer as well if not better than hydrochloric acid; but when endeavoring to obtain lower temperatures than —30° C. by previously cooling the acid, it was found that better results were obtained with hydrochloric acid.

I will add that when snow is not available I have found satisfaction in employing shaved ice for this purpose.

142.—ANALYSIS OF A HAND FIRE GRENADE.

By Chas. Catlett and R. C. Price.

The analyses of several of these " Fire Extinguishers " have been published, showing that they are composed essentially of an aqueous solution of one or more of the following bodies : sodium,

potassium, ammonium and calcium chlorides and sulphates, and in small amount borax and sodium acetate; while their power of extinguishing fire is but three or fourfold that of water.

One of these grenades of a popular brand of which I have not found an analysis was examined by Mr. Catlett with the following results: The blue corked flask was so opened as to show that it contained no gas under pressure, and upon warming its contents, but 4 or 5 cubic inches of a gas were given off. The grenade contained about 600 cc. of a neutral solution, which gave on analysis :

	In 1000 cc. grams.	In the Flask. grains.
Calcium chloride[1]	92.50	850.8
Magnesium "	18.71	173.2
Sodium "	22.20	206.9
Potassium "	1.14	10.6
	134.55	1241.5

As this mixture of substances naturally suggested the composition of the " mother liquors " from salt brines, Mr. Price made an analysis of such a sample of " bittern " from the Snow Hill furnace, Kanawha Co., W. Va., obtaining the following composition :

	In 1000 cc. grams.	In 200 cc. grains.
Calcium chloride[2]	299.70	925.8
Magnesium "	56.93	175.7
Strontium "	1.47	4.5
Sodium "	20.16	62.2
Potassium "	5.13	15.8
	383.39	1184.0

There is of course some variation in the bittern obtained from different brines, but it appears of interest to call attention to this correspondence in composition, as indicating that the liquid for filling such grenades is obtained by adding two volumes of water to one of the " bittern." The latter statement is fairly proven by the presence of the bromine, and certainly from an economical standpoint such should be its method of manufacture.

[1] Trace of bromide.   [2] Trace of bromide.

NOTES ON PURPUROGALLIN.

BY SAMUEL C. HOOKER.

I recently observed that purpurogallin is formed in considerable quantities by the action of potassic ferricyanide on pyrogallol, and, consequently, made a few experiments to ascertain whether a better yield would result from the use of this oxidising agent than had been heretofore obtained. The great interest aroused in purpurogallin by Nietzki and Steinmann's important investigation[1] is a sufficient reason for communicating the results of these experiments, especially as I believe the method of oxidation about to be described is more satisfactory than any thus far published.

Eighty-seven grams of potassic ferricyanide are dissolved in 330 cc. of cold water, the solution filtered if necessary, and added at one operation to 20 grams of pyrogallol also dissolved in 330 cc. of cold water. Almost immediately gas is evolved, the solution loses its rich red color, and purpurogallin separates. At the end of half an hour the oxidation is complete, and the purpurogallin is filtered off, washed well with water, and dried. A yield of 13.5–14 per cent. of the weight of the pyrogallol employed can be thus obtained.

On standing, the solution deposits a further quantity of purpurogallin; this, however, is very small, and is less pure than that first obtained.

By increasing the quantity of potassic ferricyanide a somewhat larger yield can be obtained, but the purpurogallin is not as pure as when made according to the above directions.

An interesting fact, not previously observed, I believe, is the formation of purpurogallin by the oxidation of gallic acid. If a small quantity of potassic nitrite be added to a cold aqueous solution of gallic acid, the solution darkens and bubbles of gas escape. On shaking out with ether, evaporating the extract to dryness and treating the crystalline mass thus obtained with cold water, a substance resembling purpurogallin in its appearance and properties is left undissolved.

On the addition of a trace of nitric acid to purpurogallin dissolved

[1] Berichte der deutsch. chem. Gesell. **20,** 1277.

in concentrated sulphuric acid, the red color of the solution gives place to an intense violet. This reaction is extremely delicate and beautiful. With minute traces of the substance, the test is best effected by dissolving in sulphuric acid on a watch-glass and exposing for a minute or two to the fumes escaping from concentrated nitric acid. The violet color produced soon fades away. The addition of potassic nitrite to the sulphuric acid solution also gives the same intense violet.

Contributions from the Laboratory of the New York Agricultural Experiment Station.

III.—SUGARS AND STARCH IN FODDERS, AND THEIR DETERMINATION.

By E. F. LADD.

There seems to have been but a limited number of determinations made of the percentage of sugars and starch in our numerous feeding stuffs; and during the past year I have had occasion to determine the amount in a large number of products. Some time has also been devoted to a comparison of available methods, the results of which are first considered.

Freshly prepared diastase with wheat and its products and corn meal gave an amount of starch, as determined by Fehling's solution, comparing favorably with that obtained by inversion with acid; but with hays and similar products I failed to secure any appreciable action of the diastase upon their starch content, thus rendering the method worthless for my purpose.

I then turned my attention to the inversion of the starch by means of acid, and found both hydrochloric and sulphuric acids recommended; and in order to determine which would serve my purpose best I made several parallel trials with the two acids upon starch and a number of feeding stuffs. By these preliminary trials I found that with starch rather higher results were obtained by the use of sulphuric acid, but that with hays and fodders in general

4

more uniform and slightly higher figures were obtained by the use of hydrochloric acid. In all these trials five grams of fodders or three grams of starch were used and 150 cc. of distilled water.

Several comparative trials were made for the most complete inversion of fodders by heating the contents in bottles tightly corked and in flasks carrying a long glass tube to serve as a condenser, but could see no appreciable difference in the results obtained upon fodders by the two methods.

Several trials were made to determine the amount of acid to use, also the time necessary for the conversion of the starch. The amount of starch inverted increased with each addition of acid up to from 3 to 5 cc. for different fodders; above this quantity up to 10 cc. no higher results were obtained than when 5 cc. were used. Several trials showed that at the end of eleven hours as much was inverted as could be obtained by prolonged heating up to fourteen hours. In order to secure uniform results with the fodders under examination I proceeded as follows:

Five grams of substance were brought upon a filter and washed with distilled water, in small quantities at a time, until the washings amounted to 200 cc. The residue[1] was dried for the starch determination. The sugar, as glucose or invert sugar, was then determined by means of Fehling's solution in 10 cc. of the filtrate. Another portion of the above washings was heated with hydrochloric acid on the water-bath for one half hour, then neutralised with sodium carbonate and the sugar determined as in the first; the difference between the two determinations being taken as sucrose or water soluble matter inverted by the acid.

The residue from the sugar determination was put in an Erlenmeyer flask of about 250 cc. capacity with 150 cc. of distilled water and 5 cc. of concentrated hydrochloric acid, and the flask closed by a cork carrying a small glass tube three and one-half feet in length, to act as a condenser. The flask was then set in a water bath kept at 100° C. for 12 hours, then allowed to stand until the following morning, filtered, made slightly alkaline with sodium carbonate, the filtrate made up to 200 cc., and the sugar determined by Fehling's solution. The starch is then easily calculated, or better by taking the readings for starch directly from a plotted chart.

[1] In a few of the earlier determinations a separate quantity of substance was taken for the starch and the sugars were deducted; but this requires unnecessary calculations, as well as being more liable to error.

In the following table are given the result of a few of the determinations for our most common feeding stuffs. In a few instances among the earlier determinations the whole was determined as starch and are so given. A few notes concerning the substances examined may be essential for a better understanding of the condition of the fodders at time of examination.

No. 1. The sample of fodder corn was taken from a lot used for ensilage.

No. 2 was taken from the field after the corn had been harvested.

No. 3 was sorghum cut for the silo.

Nos. 5 and 6 were each the average for 21 determinations at time of full bloom.

No. 7 was comfrey taken in early bloom.

No. 8 was a sample of prickly pear from Texas, cut in April.

No. 9 was the stump from same source as last, but cut at a later date.

Table Showing Percent. of Sugars and Starch in Fodders.

No.	Substance.	Invert Sugar.	Sucrose.	Starch.	Percent. of Nitrogen-free Extract as Sugars and Starch.
1	Fodder corn	9.00	0.40	13.87	53.48
2	Corn fodder	2.50	1.43	22.88	53.32
3	Sorghum	17.60	3.40	12.19	64.21
4	Alsike clover	...	...	14.63	33.81
5	Red clover, average for 21	3.88	2.48	9.38	35.40
6	Timothy, average for 21	2.23	6.21	19.72	55.69
7	Prickly comfrey	6.22	0.80	8.14	33.87
8	Cactus, top	0	5.92	9.96	30.00
9	Cactus, stump	2.80	3.60	17.10	41.12
10	Meadow hay	...	...	24.32	49.32
11	Wheat straw	...	...	22.42	59.52
12	Oat straw	...	...	23.18	51.14
13	Oats	...	...	53.20	81.05
14	Wheat	1.64	2.36	57.91	76.37
15	Wheat flour	3.64	8.36	61.88	86.77
16	Wheat middlings	3.20	6.40	41.44	75.31
17	Wheat bran	1.60	4.40	45.60	83.53
18	Ship Stuff	2.08	5.92	41.46	83.07

In the twenty-one determinations included in No. 5 for red clover the following were the variations :

	Maximum.	Minimum.
Invert sugar	5.20	2.60
Sucrose	3.80	1.20
Starch	13.90	5.58

With the timothy in the average for the 21 determinations the following for the highest and lowest were found:

	Maximum.	Minimum.
Invert sugar	5.00	2.40
Sucrose	7.60	4.68
Starch	22.61	17.55

A few determinations of the sugars and starch were made in timothy hay taken from the plats at time of full bloom, and again with samples taken from the same plats after the seeds were formed, but before they were fully matured.

The results[1] are given in the following table:

Plat.	Timothy.				Invert Sugar.	Sucrose.	Starch.	Percent. of Nitrogen-free Extract as Sugars and Starch.
VI	Early cut	.	.	.	3.60	6.36	22.61	62.08
VI	Late cut	.	.	.	2.60	4.00	22.38	55.39
XV	Early cut	.	.	.	3.72	5.96	18.07	52.73
XV	Late cut	.	.	.	2.32	5.40	21.66	60.24
XIX	Early cut	.	.	.	3.04	4.68	19.45	52.46
XIX	Late cut	.	.	.	2.00	5.20	22.61	55.69

Here we find that as the hays approached ripeness the percent. of sugars was diminished, while the starch increased.

A plot uniform in appearance in the grass fields was divided into several small plats, and various fertilizing ingredients applied as a top dressing in the spring, the purpose being to study the influence of fertilizers upon the composition of timothy grass, and the results for a few of the determinations of sugars and starch are given in the following table:

Plat.	Fertilizer.	Invert Sugar.	Sucrose.	Starch.	Percent. of Nitrogen-free Extract as Sugars and Starch.
I	Sulphate of potash .	2.40	5.88	21.20	53.05
II	Sulphate of ammonia	2.76	7.20	19.19	54.74
III	Acid phosphate . .	3.92	5.80	19.00	56.27
XIII	Lime	5.00	7.32	18.96	60.61

[1] From Agricultural Science **1**, No. 10, 222.

Plat.	Fertilizer.	Invert Sugar.	Sucrose.	Starch.	Percent. of Nitrogen-free Extract as Sugars and Starch.
XIV	Gypsum	3.56	5.36	20.52	54.98
XV	Nothing	3.72	5.96	18.67	52.73
XVII	Sodium nitrate . .	3.44	5.56	20.63	56.76
XVIII	Sulphate of ammonia	3.20	6.20	17.78	51.00
XIX	Muriate of potash .	3.04	4.68	19.45	52.46
XX	Sulphate of potash .	2.96	6.00	19.72	52.79

From the preceding table we can trace no relation between the percent. of sugars and starch and the kind of fertilizer applied to the soil, nor can we say that a potash dressing increased the starch content of the timothy, as some have claimed would result from such an application.

In a study of the composition and variation in our feeding stuffs from year to year, the determination of the sugars and starch will be made, to see whether the general results of one season will be confirmed in the following year, or whether as great variation will occur as has been found for the albuminoids of grass in two successive years.

GENEVA, N. Y., *Oct.* 12, 1887.

AN IMPROVED FORM OF GAS APPARATUS.

By J. T. WILLARD.

The description of an improved form of Elliott's apparatus for gas analysis, by J. B. Mackintosh,[1] recalls one devised by the writer. It was constructed for use in the chemical laboratory of the State Agricultural College of Kansas, and was used in an examination of the natural gases of that State by Prof. G. H. Failyer. As it embodies some advantages not combined in any other apparatus that has come under the notice of the writer, a description of it may not be amiss. It is essentially a combination of Elliott's apparatus and Frankland's apparatus for the analysis of gases

[1]This Journal 9, 294.

incidental to water analysis,[1] with important modifications and additions. The accompanying cut will make its construction clear.

A is a pressure tube graduated in millimetres. *B* is the measuring tube holding about 120 cc., 100 cc. of which is graduated to tenths, beginning with the stopcock *F*. Its upper part is narrow, thus admitting accurate measurement of small amounts of gas as well as large. It is enclosed in a water jacket which must be provided with some means of securing a uniform temperature throughout. *C* is the explosion tube and is ungraduated. *D* is the absorption tube surmounted by a funnel for the introduction of reagents. *E* is a laboratory vessel of the ordinary kind which may be attached instead of *D* if desired. It is obvious that any form of absorption pipette may be attached at *f*. *B*, *C* and *D* are connected by the stopcock *F*, a four-way cock shown in section above. By means of this cock, the others being suitably arranged, either tube may be put in connection with either of the others or with the external air, without disturbing the other tube or tubes. *G* is an ordinary three-way cock. Reservoirs not shown in the cut are attached to the tubes by means of rubber tubing at *a*, *b* and *c*. The ends of the tubes are closed by rubber stoppers, and the several parts are connected by heavy rubber connectors at *d*, *e*, *f*, and *g*. The ends of the capillary tubes are ground squarely at these joints so that they come together perfectly. The apparatus is firmly attached to a suitable support, such as any one with a little ingenuity may devise. It is essential that *A* and *B* be so supported that their relative position shall remain unaltered. The apparatus was designed for use with mercury, but water may be used. With water the pressure tube would be unnecessary.

Concerning the mode of operating the apparatus but little need be said. It is most convenient to use Frankland's method of measuring, in which the gas operated upon is always brought to the same volume, or to an aliquot part of the original volume, by adjusting the pressure of the mercury in *A*. Points on the pressure tube corresponding to a number of convenient volumes in the measuring tube must be previously determined with care. The tensions exerted by varying amounts of gas brought to the same volume will be proportional to the amounts of gas present. If the gas is brought to an aliquot part of the original volume, the tension
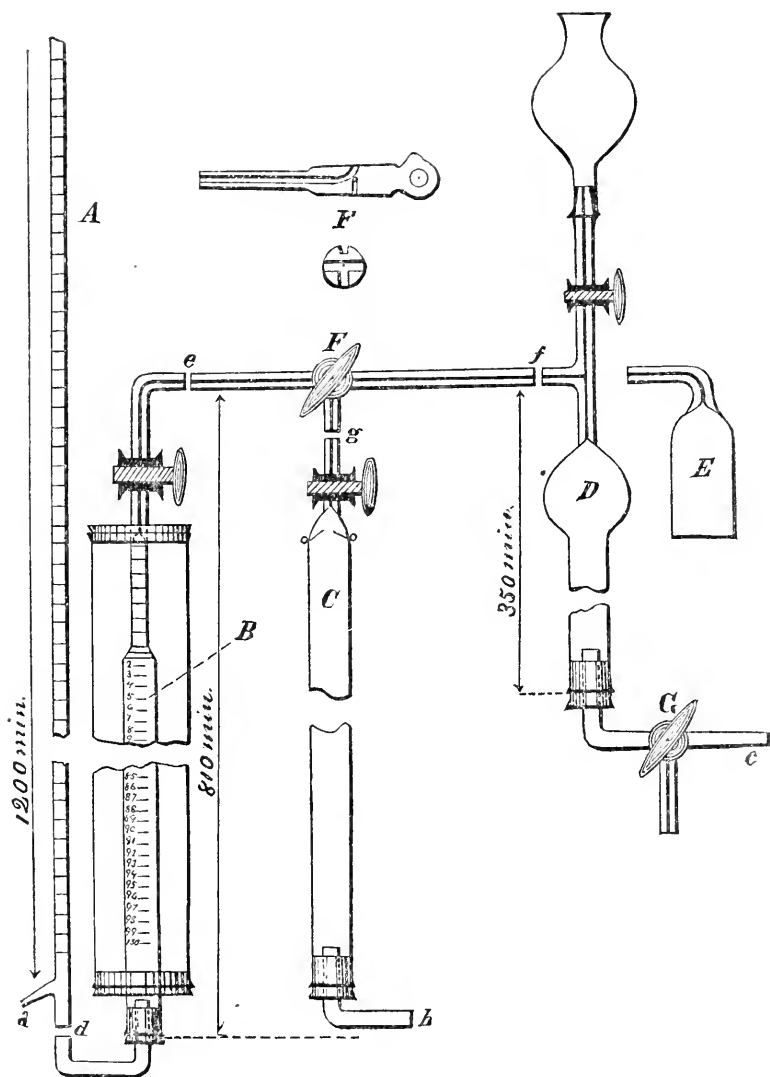
found may be reduced to that corresponding to the original volume by a very simple calculation.

The explosion of the gases is performed under reduced pressure according to the principles developed by Thomas.[1] This method of explosion is very advantageous and may be used with this apparatus, even if water is used in the tubes B and D, by filling C with mercury. On lowering the reservoir connected with C any desired degree of rarefaction may be produced. It is convenient to have a rough scale back of C and extending below, for use in measuring the pressure under which the gas is confined during explosion.

The fourth way in the stopcock F is essential for the discharge of the reagents employed in D; it is also used for the introduction of the gases. If it is desired to preserve a portion of the gas in D while another portion is being measured and exploded in B and C, it is necessary to close this external opening of F. This may be done simply and perfectly by filling the way with water or mercury from one of the tubes, and then slipping a short piece of rubber tubing filled with water over the end of the stopcock and closing it with a clamp.

I think no other details of manipulation need be entered into, as they are similar to those already described for other apparatus, or can be readily worked out by the operator.

The apparatus may be used for certain of the purposes to which the nitrometer has been put, such as the valuation of bleaching powder by hydrogen peroxide and *vice versa*.

The apparatus described was made in most excellent manner by Mr. Emil Greiner, of New York.

[1] Jour. Chem. Society **35**, 213.

ON THE FATTY ACIDS OF THE DRYING OILS.

By L. M. Norton and H. A. Richardson.

Linoleic acid was first carefully examined by Schüler,[1] who prepared it from linseed oil, and who ascribed to it the symbol $C_{16}H_{28}O_2$. Subsequent investigators accepted this symbol until a new investigation was made a few months since by Peters.[2] He isolated the acid with great care, and his analyses gave figures which agree with a symbol of $C_{18}H_{32}O_2$, and he found that by heating the linoleic acid with iodohydric acid he obtained stearic acid, confirming thus the symbol which he allots to it. Hazura[3] has confirmed Peters' results.

We have made a new preparation according to Schüler's method, and we find that the greatest care must be exercised in the preparation of the acid, owing to the extraordinary ease with which the acid takes up oxygen. Analysis of our acid gave the following results:

	I.	II.	III.	Theory for $C_{16}H_{28}O_2$.	Theory for $C_{18}H_{32}O_2$.
C	77.00	76.97	77.03	76.18	77.14
H	11.41	11.23	11.20	11.11	11.42

These results seem to confirm Peters' experiments, although the hydrogen still remains in doubt. We also repeated the reduction of the linoleic acid with iodohydric acid, but with different results. We obtained an acid which melted constantly at 83°, and gave the following figures upon analysis:

	I.	II.	Theory for $C_{18}H_{36}O_2$.	Theory for $C_{18}H_{36}O_3$.
C	72.07	72.20	76.05	72.00
H	13.01	12.50	12.67	12.00

At this point we were led to make an observation concerning linoleic acid which we hope may throw much light eventually on the chemistry of the drying oils. We found great difficulty in drying linoleic acid, and were finally forced to use a desiccator containing sulphuric acid, and a glass coil through which steam could be passed. By placing the watch glass containing the acid upon the coil we hoped to dry easily the acid. A current of hydrogen was passed constantly through the apparatus to prevent

[1] Ann. d. Chem. **101**, 252.   [2] Monatshefte f. Chem. **7**, 552.   [3] Monatshefte f. Chem. **7**, 637.

oxidation.   To our astonishment, we were unable to obtain a
constant weight, but the acid lost in weight to such an extent that
in sixty-eight hours 20.36 per cent. of the original acid had
disappeared.   The ratio of decrease was regular throughout the
whole time.   Analysis showed that no change whatever had taken
place in the composition of the substance during this time.   It
was evident that the acid had volatilised.

Distillation Product from Linoleic Acid.

The acid was next subjected to distillation at a reduced pressure.
At about 290° at a pressure of 89 mm. a beautiful colorless product,
comprising about three-fourths of the original acid, was obtained.
A residue remained in the flask which has not been examined.
Once prepared, the acid distills without leaving a residue.   There
was no evidence of decomposition during the first distillation.   The
product possesses a specific gravity of 0.9108 at 15° as compared
with water at 4°.   Several preparations were made and analysed
with the results given below :

	I.	II.	III.	IV.	Theory for $C_{18}H_{25}O_2$.	Theory for $C_{20}H_{34}O_2$.	Theory for $C_{20}H_{36}O_2$.
C	78.04	77.81	78.08	78.13	76.18	78.43	77.93
H	11.39	11.81	11.57	11.73	11.11	11.11	11.67

It was found also by analysis that the first and last portions
which distilled were identical in composition.   The distilled acid
absorbs bromine with great violence.   We attempted the determi-
nation of the vapor density of the acid, and constructed a modifica-
tion of Victor Meyer's vapor density apparatus, which will be
described elsewhere, allowing the vapor density of bodies with a
very high boiling point to be taken at any desired reduction of
pressure, and obtained the following results for the distilled acid :

			Theory for $C_{20}H_{36}O_2$.	Theory for $C_{18}H_{32}O_2$.
Vapor density	151.1	152.7	154.	140.

A barium salt of the distilled acid was prepared by dissolving it
in alcohol, neutralising with ammonia, and precipitating with
barium chloride.   The salt was rendered anhydrous by heating
above 100° in an atmosphere of hydrogen, and a barium estima-
tion made :

		Theory for $Ba(C_{20}H_{35}O_2)_2$.	Theory for $Ba(C_{18}H_{31}O_2)_2$.
Ba	18.04	18.24	19.71

These results cause us to coincide with the opinion formed by Hazura and Friedreich[1] from an examination of the action of bromine and oxidising agents upon linoleic acid, that linoleic acid, so called, is a mixture of acids. We shall investigate further these distillation products.

Ricinoleic Acid.

The volatility of linoleic acid led us to expect a similar volatility in ricinoleic acid, and our expectations were realised. The acid was prepared by the method of Saalmüller,[2] and after careful purification, analysis furnished the following results:

	I.	II.	Theory for $C_{18}H_{34}O_3$.
C	72.52	72.49	72.48
H	11.51	11.36	11.41

The specific gravity of the acid was 0.9502 at $15°$ compared with water at $4°$. This acid was subjected to distillation at a pressure of 20 mm. A liquid of a light yellow color came over freely between $240°$ and $260°$, while a non-volatile residue constituting about one-fourth of the original acid remained in the flask. This residue solidified upon cooling. The liquid was an acid, and possessed the specific gravity of 0.912. After redistillation the analysis gave:

	I.	II.	Theory for $C_{20}H_{36}O_2$.
C	78.20	78.03	77.93
H	11.69	11.65	11.67

The vapor density of the distilled product was as below:

		Theory for $C_{20}H_{36}O_2$.
Vapor density	150.1	154.

This product appears at the present time to be identical with that furnished by the distillation of linoleic acid. It will be further investigated. We are led to believe that ricinoleic acid also is not a homogeneous substance. We propose to examine the distillation products of the acids of the drying oils.

INSTITUTE OF TECHNOLOGY, BOSTON.

[1] Monatshefte f. Chem. **8**, 164.   [2] Ann. d. Chem. **64**, 108.

XXXI.—ON THE OCCURRENCE IN NATURE OF COPPER ANTIMONIDE.

BY A. LAIST AND T. H. NORTON.

Combinations of copper and antimony have hitherto been known only in the form of the four alloys prepared by Calvert and Johnson,[1] and Christofle.[2] Recently a large deposit of an antimonide of copper has been discovered in the eastern part of Asia Minor, not far from Mytilene. We are indebted to the courtesy of Mr. Archag Melcon for samples taken from an extensive vein underlying the entire area of a Turkish village, and easily accessible from the surface.

The new mineral resembles native silver in color. The freshly fractured surface is quite lustrous, but tarnishes easily, especially in air containing sulphuretted hydrogen. It is of massive structure; no traces of crystallisation or distinct planes of cleavage being detected. It is quite brittle, with very uneven fracture, and in hardness it stands between fluor spar and apatite, *i. e.* on the scale 4–5. The fusibility in the reducing flame lies between that of antimony glance and of natrolite.

The high specific gravity of the mineral is its most striking physical characteristic. This was found to be 8.812 as the mean of three closely agreeing determinations. It is worthy of note that but a limited number of minerals possess a higher specific gravity.

A qualitative examination showed the sample of the mineral to be a perfectly pure compound of copper and antimony, free from other metals, and also free from gangue.

The quantitative analyses gave the following results:

	I.	II.	III.	Average.
Cu	73.45	73.74	72.92	73.37
Sb	27.05	26.90	26.62	26.86
	100.50	100.64	99.54	100.23

The analytical results give figures lying between those required

[1] Phil. Mag. (4) **18**, 354.

[2] Combinaisons de l'antimoine avec les métaux. Göttingen, 1863.

by the two simple molecular expressions Cu_5Sb and Cu_6Sb, and approximate still more closely to the combination $Cu_{11}Sb_2$.

Cu_5Sb.	Cu_6Sb.	$Cu_{11}Sb_2$.	Found.
72.42	75.6	74.39	73.37
27.58	24.4	25.61	26.86

It will be seen that the composition of this copper antimonide is not far removed from the stibio hexargentite variety of dyscrasite, the only native antimonide hitherto known, which Petersen[1] has shown to exist in two well defined forms, Ag_3Sb and Ag_6Sb.

It seemed a matter of interest to prepare an artificial alloy of copper and antimony of the same composition as the mineral just described. Accordingly two hundred grams of copper and seventy-four grams of antimony were fused together in a clay crucible and allowed to cool slowly. The regulus obtained weighed a few decigrams less than two hundred and seventy-four grams, and its composition therefore was copper 73 per cent., antimony 27 per cent.

In appearance it closely resembled the native mineral, although not quite so lustrous. It was also more brittle, probably on account of a more rapid congelation. The specific gravity was 8.829; very slightly higher than that of the mineral, 8.812.

It may be mentioned in this connection that the specific gravity of this antimonide is notably higher than the theoretical figure for a mixture of copper and antimony in the proportions given, viz. 8.19, the difference being 0.622.

A similar fact was noticed by Calvert and Johnson[2] when experimenting on a combination of the two metals represented by the formula $CuSb$. The specific gravity found was 7.99, while that calculated was 7.38; difference 0.61.

With regard to the metallurgical utilisation of the large Asiatic deposit of this copper antimonide, it is doubtful whether the expense attendant upon the separation of the two metals would permit of successful competition on the one hand with stibnite and on the other hand with the abundant American deposits of copper minerals. Probably the simplest method of treating the mineral would be to expose it to the action of hot dilute sulphuric acid, which would dissolve out the copper and leave an insoluble

[1] Pogg. Ann. **137**, 377.   [2] Phil. Mag. (4) **18**, 354.

residue of antimony oxide. Experiment shows us that if an excess of the acid be avoided, all of the copper is extracted and but a slight amount of antimony enters into solution.

Several alloys containing copper and antimony are used in the arts, and the mineral on account of its purity could be used directly in their preparation.

This new mineral is named horsfordite, in honor of Professor Horsford, formerly Rumford Professor of Chemistry at Harvard University.

XXXII.—ON A NEW APPARATUS FOR FRACTIONAL DISTILLATION.

By T. H. Norton and A. H. Otten.

In his ingenious apparatus for the technical transformation of ammonium sulphocyanide into calcium sulphocyanide (Wurtz, Dictionnaire de Chimie, Supplément, p. 597), Dr. J. Tcherniac introduced an interesting feature, the so-called *déverseur*, designed primarily to prevent the frothing accompanying the rapid distillation of the ammoniacal liquor. This *déverseur* consisted simply of a cylinder about two-thirds of the size of the retort containing the mixture of lime and solution of ammonium sulphocyanide, and was situated above this retort. The bottom of the cylinder was connected by a pipe with the bottom of the retort, while pipes from the upper portion connected with the top of the retort and with the condensing apparatus. The practical result of this arrangement was that the vapors from the retort entered the top of the cylinder by one opening, and left it by another opening for the condenser, while all liquid carried along mechanically, dropped to the bottom of the cylinder and returned to the retort.

Distillation is carried on so easily and rapidly by means of this device that it seemed a matter of interest to experiment upon the adaptation of this principle of construction to the wants of the laboratory in the form of an apparatus for fractional distillation. We are indebted to Dr. Tcherniac for a glass model embodying the essential features of the apparatus just described, the details of which will be easily understood from the accompanying cut.
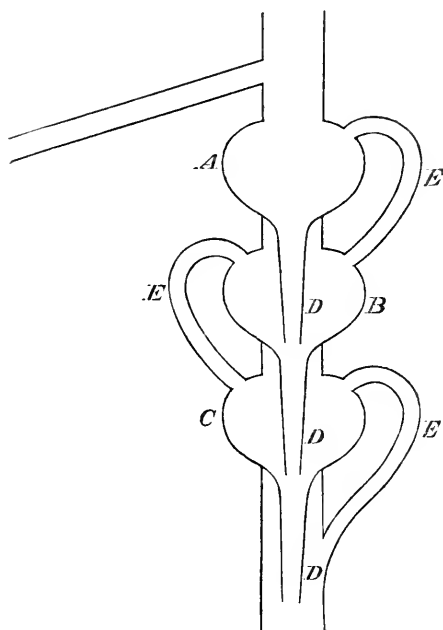
The three bulbs *A*, *B* and *C* are connected with each other by
the curved tubes *E E E*, the lowest connection entering the stem of
the apparatus. Small tubes *D D D*, 2 mm. in diameter, likewise
project from the bottom of each bulb. Their capillarity is increased
by passing a platinum wire through the entire series. When the
device is inserted into a distilling flask, it will be seen at once that
the current of vapor takes a zig-zag course, passing through the
tubes *E E E*, and across the top of each bulb, while all condensed
liquid returns directly by the route of the tubes *D D D* into the
distilling flask. A fractional distillation performed by means of
this apparatus would hence be conducted on principles directly
contrary to those which underly the construction of our ordinary
technical and laboratory stills, in which the central object is to bring
the ascending current of vapor into as intimate contact as possible
with the downward flow of liquid resulting from the condensation
of less volatile constituents.

In order to test the availability of the new design we brought it
into direct comparison with two well known types of fractionating
apparatus, viz. those of Hempel and of Linnemann, both based on

the ordinary principle of a thorough washing of the vapor current by the products of partial condensation.

The Linnemann apparatus used consisted of a tube 1 cm. in diameter, with three bulbs blown along a space of 16 cm., and contained three cups of platinum gauze. The Hempel apparatus consisted of a similar tube, the cups being replaced by a layer of glass beads 7 cm. deep.

The new device contained three bulbs blown on a tube 1 cm. in diameter along a space of 12 cm. as described above. Comparative fractional distillations were conducted with several mixtures of known quantities, every precaution being taken to render the conditions identical in the different series. In all cases 100 cc. of liquid were used, and the fractions were collected at intervals of 3° in graduated cylinders. After each addition, during the fractionation, of a new quantity of liquid, fractions were collected during the two preceding temperature intervals.

The quantities given are in cubic centimetres. The first column, A, gives the results obtained with the Linnemann apparatus ; the second column, B, those with the Hempel apparatus, and the last column, C, those with the new apparatus.

First Series.

Mixture of 50 cc. of acetone (96 per cent.), boiling point 56°–57°, and 50 cc. of methyl alcohol, boiling point 66.6°.

First Fractionation.

	A.	B.	C.
56–59°	31	40	33
59–62	46	38	39
62–65	14.5	12.5	16.5
65–67	8	8.5	11
	99.5	99	99.5

Second Fractionation.

	A.	B.	C.
56–59°	46.5	53	47.5
59–62	28	24.5	23.5
62–65	8	9.5	11
65–67	14.5	11.5	16.5
	97	98.5	98.5

Third Fractionation.

	A.	B.	C.
56–59°	51	58.5	50.5
59–62	19.5	18.5	18
62–65	6.5	8	7.5
65–67	18	13	20
	95	98	96

Fourth Fractionation.

	A.	B.	C.
56–59°	57	61.5	55
59–62	11.5	13	13.5
62–65	6.5	7.5	6
65–67	18	14.5	21
	93	96.5	96.5

Fifth Fractionation.

	A.	B.	C.
56–59°	58	63	55.5
59–62	9.5	12.5	12
62–65	5	5.5	4.5
65–67	20	14.5	24.5
	92.5	95.5	94.5

SECOND SERIES.

100 cc. crude wood alcohol.

First Fractionation.

63–66°	48	45.5	46.5
66–69	30.5	33	31.5
69–72	12.5	16.5	13
72–75	4	1.5	6.5
75+	2.5	1	2
	97.5	97.5	99

Second Fractionation.

63–66°	57	50.5	52.5
66–69	26	30	27
69–72	6	12.5	11.5
72–75	3.5	1.5	4
75+	3.5	0.5	3.5
	96	95	98.5

Third Fractionation.

63–66°	60	56.5	61
66–69	24.5	30	21.5
69–72	6	6	8
72–75	2	1	2
75+	3	0.5	4.5
	96	94	97

Fourth Fractionation.

63–66°	70.5	64.5	71
66–69	16	21.5	14
69–72	3.5	6.5	5.5
72–75	2	1	2
75+	3	0.5	3.5
	95	94	96

Fifth Fractionation.

63–66°	74.5	65.5	75.5
66–69	13	20.5	11
69–72	3.5	6	5
72–75	1	1	1
75+	3	0.5	3.5
	95	93.5	96

5

THIRD SERIES.

Mixture of 50 cc. of ethyl alcohol, boiling point 78.3°, and 50 cc. of water, boiling point 100°.

First Fractionation.

	A.	B.	C.
79–82°	27	29.5	27
82–85	16.5	16.5	18
85–88	8	8.5	6.5
88–91	5	5	5
91–94	6	3.5	4
94–97	3.5	3.5	4.5
97–100	32	31.5	32
	98	98	97

Second Fractionation.

	A.	B.	C.
79–82°	33	42.5	39
82–85	13.3	7	8.5
85–88	4.5	4	5
88–91	4.5	2.5	3.5
91–94	1	1.5	2.5
94–97	1.5	1	1.5
97–100	39.5	38	38
	97	96.5	97

Third Fractionation.

	A.	B.	C.
79–82°	43.5	46	43
82–85	4.5	4.5	6
85–88	4	3	3.5
88–91	0.5	1	2
91–94	0.5	0	0.5
94–97	0.5	1	0.5
97–100	41.5	41	41
	95	96.5	96.5

Fourth Fractionation.

	A.	B.	C.
79–82°	46.5	49	47
82–85	4	3	4
85–88	2	2	2.5
88–91	0	0	0.5
91–94	0	0	0
94–97	0.5	1	0.5
97–100	42.5	41	42
	95.5	96	96.5

Fifth Fractionation.

79–82°	50	51	49
82–85	1.5	2	3.5
85–88	0	0.5	0
88–91	0	0	0
91–94	0	0	0
94–97	2	2	1.5
97–100	43	40.5	42.5
	96.5	96	96.5

FOURTH SERIES.

Mixture of 50 cc. of toluene, boiling point 110°, and 50 cc. of amyl alcohol, boiling point 131°.

First Fractionation.

	A.	B.	C.
108–111°	40	42.5	43
111–114	20.5	19.5	15.5
114–117	6	9	9.5
117–120	2	4	5.5
120–123	2	5	4.5
123–126	5	4	4.5
126–129	22.5	14	16
	98.5	98	98.5

Second Fractionation.

	A.	B.	C.
108–111°	49	42.5	47
111–114	8.5	11.5	10
114–117	4	7	6.5
117–120	3.5	5	4
120–123	3	4	3.5
123–126	3.5	4	3
126–129	26	23	23
	97.5	97	97

Third Fractionation.

	A.	B.	C.
108–111°	50	44	50
111–114	6	9.5	7
114–117	3.5	5.5	4
117–120	2.5	4	2.5
120–123	2.5	4	2
123–126	1.5	3.5	4.5
126–129	31	27	26
	97	97.5	96

Fourth Fractionation.

	A.	B.	C.
108–111°	52	48.5	53
111–114	4	5.5	3.5
114–117	2.5	7	3
117–120	2	1.5	3
120–123	1.5	3	3.5
123–126	1.5	3	1.5
126–129	33	29	27.5
	96.5	97.5	95

Fifth Fractionation.

108–111°	53	47.5	55
111–114	3.5	7.5	3
114–117	3	3	2.5
117–120	0.5	4	1.5
120–123	0.5	1	1
123–126	2.5	2.5	1.5
126–129	34	31	31
	97	96.5	95.5

FIFTH SERIES.

Mixture of 50 cc. of benzene, boiling point 80.5°, and 50 cc. of toluene, boiling point 110°. (In this series the Linnemann tube

(A) was provided with six platinum gauze cups, instead of three, as in the preceding series.)

First Fractionation.	A.	B.	C.
81–84°	30	25	20
84–87	8	10.5	13
87–90	11	8	7
90–93	5	10.5	10
93–96	4	4	6.5
96–99	3	5	8.5
99–102	3	4	5
102–105	7.5	5.5	5
105–108	10	9	7
108–111	13	14.5	14
	94	96	96

Second Fractionation.	A.	B.	C.
81–84°	32	37	28
84–87	10.5	7	6.5
87–90	5	6.5	6.5
90–93	5	4	6.5
93–96	3	1	6
96–99	2.5	3.5	5
99–102	2	4	4.5
102–105	4.5	5	6.5
105–108	6	6.5	7
108–111	21	20	18
	91.5	95	94.5

Third Fractionation.	A.	B.	C.
81–84°	38	39	32
84–87	3.5	6	5
87–90	5	4	6
90–93	4	3.5	5.5
93–96	3	1.5	4.5
96–99	2	2	2
99–102	1	3	3.5
102–105	2	4.5	4.5
105–108	4.5	5.5	6.5
108–111	27	23	24
	90	93	94

Fourth Fractionation.	A.	B.	C.
81–84°	41	41.5	34.5
84–87	4	4	5
87–90	4	3	4.5
90–93	3	4	4.5
93–96	2.5	2	2.5
96–99	0.5	2	3.5
99–102	1	1	2.5
102–105	2.5	2.5	3.5
105–108	3.5	4	4
108–111	29	26	27
	90	90	91.5

Fifth Fractionation.			
81–84°	43	44.5	37
84–87	3	3.5	3.5
87–90	2	2.5	3.5
90–93	1	1	2.5
93–96	0	1	2.5
96–99	2.5	1	2
99–102	0	1.5	1.5
102–105	2.5	2.5	2.5
105–108	5.5	3.5	5
108–111	28	28.5	28.5
	88	89.5	88.5

These experimental data are of interest as showing that no one form of apparatus is superior to other forms for all cases. Thus in the series of distillations of mixtures of acetone and methyl alcohol, larger fractions of the latter constituent are separated by the use of the new apparatus than by the use of the other two forms. Hempel's apparatus yields a larger fraction at the boiling point of acetone in the above case than either of the other forms, while on the contrary, in the case of wood spirit, its initial and terminal fractions are both inferior in amount to those of the other forms. Again, in the distillation of a mixture of alcohol and water there appears to be but slight difference in the effects obtained by the three forms. In the case of a mixture of benzene and toluene, the two older structures permit the separation of decidedly larger benzene fractions, while the toluene fractions are about the same in all cases. When the toluene is mixed with amyl alcohol the new apparatus gives better results with the lower fraction than the other two forms, while it is behind them in the separation of the alcohol.

As far as the power of rapid fractionation is concerned, the new form of apparatus, while giving results quite as satisfactory as those yielded by the two types hitherto regarded as the most efficient, certainly does not exceed them in the average thoroughness of separation.

With regard to the simplicity of construction Hempel's apparatus still remains unsurpassed, while the lateral tubes of the new form render this type certainly more fragile than the original Linnemann apparatus, and place it rather in the category of such a device as that of Le Bel and Henninger.

Although the new type cannot claim advantages which should lead to its superseding the present forms of apparatus for fractional distillation, the experiments made with it show conclusively that the principle involved in its construction, of the rapid separation of vapor and condensed liquid, yields at least as satisfactory results in practice as the totally opposite principle of a continuous washing of vapor in condensed liquid.

XXXIII.—ON THE ALLOYS OF CALCIUM AND ZINC.

By T. H. Norton and E. Twitchell.

A method for obtaining an alloy of calcium and zinc was briefly described in 1860 by Caron.[1]   It consisted in heating together in a closed crucible a mixture of 3 parts calcium chloride, 4 parts zinc, and 1 part sodium.   Caron states that by this process he was able to prepare alloys containing from 10 to 15 per cent. of calcium.

With the desire of examining these alloys more closely and of testing their availability for the production of metallic calcium, the following experiments were instituted.

In three cases the proportions indicated by Caron were used. In two cases the amount of zinc was diminished by one half.   The calcium chloride was first fused, and after congelation finely powdered.   The zinc was introduced in the form of small clippings of sheet zinc, and the sodium in small fragments.   The mixture was placed in a covered French clay crucible and heated in a furnace or muffle.   When zinc flames appeared the temperature was reduced so as to cause a steady but slight volatilisation of zinc. After the lapse of 15–30 minutes the crucible was withdrawn from the fire and broken when cool.   The alloy was found at the bottom in the form of a regulus.

The determination of the calcium in the alloys was made in some cases by the use of the "cyanide method," the zinc salt being removed from the mixture of precipitated zinc and calcium carbonates by treatment with a solution of potassium cyanide.   In other cases the hydrochloric acid solution was precipitated by ammonia and ammonium sulphide and allowed to settle, when the calcium was precipitated as oxalate from an aliquot portion of the clear liquid.

Experiment I.

The mixture of 40 grams zinc, 30 grams calcium chloride, and 10 grams sodium was strongly heated for 15 minutes.   Zinc flames then appeared and the temperature was reduced.   After further heating for 15 minutes, during which time puffs of zinc vapor were given off, the crucible was removed.   The regulus weighed 18 grams.   An analysis by the cyanide method gave

Ca   2.28

[1] Comptes rendus **50**, 547.

The specific gravity was 6.8, and the melting point 360° (the melting point of zinc). This alloy was difficult to distinguish from pure zinc. It was malleable, and had the same crystalline structure as zinc. The low percentage of calcium was evidently due to the maintenance of too high a temperature during the operation.

Experiment II.

Mixture of 20 grams zinc, 30 grams calcium chloride, and 10 grams sodium. The crucible was introduced into a muffle already heated to a bright red heat. After 25 minutes the crucible was removed. A zinc flame had been apparent during the entire time.

The regulus weighed 21.6 grams.

The analysis made by the sulphide method gave

Ca   5.44

The melting point was about 640°, coinciding very closely with the melting point of potassium iodide, which was used for a comparative determination. The hardness was 3½.

Experiment III.

The same quantities were used as in the preceding experiment. The muffle was kept for 25 minutes at such a temperature that zinc flames were not evident except when the cover of the crucible was raised.

The regulus weighed 20.7 grams.

The analysis made by the sulphide method gave

Ca   6.06

The specific gravity was 6.115. Melting point about 640°. Hardness 3½. This alloy was of a shining white color and quite brittle. The lustre did not become dull in the air at the ordinary temperature. At higher temperatures, but still far below the melting point, it oxidised rapidly. It was not attacked by cold water.

Experiment IV.

The same proportions as in the first experiment were used. The crucible was heated in an open furnace for 30 minutes, zinc being sparingly volatilised during the entire time.

The regulus weighed 39.7 grams.

The analysis by the cyanide method gave

Ca   4.97

The specific gravity was 6.24. Melting point about 640°. Hardness 3½. This alloy had the same physical properties as that obtained in the third experiment. It possessed, however, a marked granular crystalline structure.

Experiment V.

The same charge was used as in the preceding experiment. The crucible was kept in the furnace for 40 minutes, a slow volatilisation of zinc being constantly maintained.

The regulus weighed 41 grams.

The analysis by the cyanide method gave

    Ca   6.36.

The specific gravity was 6.369.

The alloy closely resembled that obtained in the third experiment.

Experiments were made to obtain alloys richer in calcium by igniting samples of the alloys already described in porcelain crucibles, in a current of hydrogen so as to expel the zinc. In all cases, however, although zinc was driven off in notable amounts, still there was a proportionate loss of metallic calcium. The residual alloy rich in calcium was left in so spongy a condition that it oxidised immediately in contact with the air, and the crucibles likewise showed traces of being attacked.

The results of these experiments would tend to show that it is exceedingly difficult, if not impossible, to obtain by Caron's method zinc-calcium alloys containing more than 6–7 per cent. of the latter metal. The notable raising of the melting point, due to the addition of small amounts of calcium to zinc, is worthy of attention.

NOTES.

A Simple Method of determining Equivalents for Use with Large Classes of Students.

I do not think it advisable, generally speaking, to introduce students to equivalents, atoms, molecules, etc., until they are pretty well advanced and tolerably expert analysts. The first term's work in this laboratory is always on the metals, and the aim of the work is to accumulate results as rapidly as possible, and to familiarise the student with as many substances as possible. I believe this to be a method that prepares the mental system for theory when the time comes for it. While the freshman class were studying the action of hydrochloric acid on metals, it was noticed by some of them that some metals apparently liberated more hydrogen than others. This observation aroused considerable interest, and I thought it would be well to introduce the equivalent then and there.

The question was put as follows : *What weight of each metal will it take to liberate one milligram of hydrogen ?*

The metals chosen for experiment were iron, zinc, and aluminium. The apparatus given to each student consisted of a 3-inch evaporating dish and a common 6-inch test tube. In some cases graduated gas tubes were given out. 50 to 100 milligrams of the metal having been accurately weighed, the test tube was filled with acid (in most cases hydrochloric acid), and inverted in the evaporating dish, previously one-third filled with the same acid. The piece of metal was now quickly brought under the tube and the whole apparatus left to itself till the solution was complete. Sometimes a gentle heat was applied. Later on it was found better to put the metal in a little cup (made by cutting off $\frac{1}{2}$ inch from the lower end of a small test tube) before bringing it under the tube, thus avoiding the possibility of bubbles being carried out by the descending current of acid. When solution was complete the tube was transferred to a large jar of water and the acid displaced by water. It was then cooled to the temperature of the room.

When graduated tubes had been employed the volume could then be read directly, the necessary corrections for temperature and pressure made, and the equivalent deduced. When ordinary test tubes had been employed, the line where gas ended and water began was marked on the tube by tying a piece of fine thread round it. Water was then run in from a carefully graduated

burette till the space previously occupied by gas was occupied by water. The volume thus obtained represented the volume of gas obtained, and was corrected for temperature and pressure as usual.

I acknowledge the apparent crudeness and roughness of the process, but invite attention to the following results :

Iron.	Zinc.	Aluminium.
28.2	32.68	9.006
27.8	32.65	9.004
27.69	32.46	9.004
27.78	32.36	9.000
27.74	32.52	9.000
27.75	32.40	9.03
27.93	32.60	8.995
28.03	32.45	8.988
28.11	32.48	9.07
27.90	32.35	8.887
27.89	32.50	9.100
27.80	32.39	9.12
27.85	32.22	9.010
27.97	32.62	
	32.46	

In some cases duplicate results are given, but where two results are identical, they are given because they were separate results obtained by different students.

In such a crude process there are so many apparent sources of error that space would forbid a discussion of them, and I will only say that I believe the small quantities operated on cause many errors to vanish. The materials were all the purest obtainable. Great care was taken in marking and reading volumes. When heat had been used, and indeed in almost every case, the tube was, after the acid had been displaced by water as previously stated, shaken so as to absorb most of the hydrochloric acid volatilised. The gas was usually allowed to stand for some time before being read. The burettes had been carefully compared with a calibrated standard, and any error in any one of them was not large enough to have affected the results materially.

There is of course nothing new about the process, but I have never seen any published results of its use with large classes.

Most of the work as to finding the best way of carrying out the process has been done by my Freshman class, some of whom have attained considerable skill in working it. The process as here presented is the best we have done so far.

When graduated tubes were employed the results were not as good. I think it was because the volume of gas and quantity of metal were great enough to be more appreciably affected by the inherent errors of the process. It should be said that the level of

the water in the tube was always brought to the level of the water in the jar before reading the volume, and that the tube was left standing long enough to get to the temperature of the room after being placed in position.

<div align="right">

JOSEPH TORREY,

Professor of Chemistry in Iowa College.

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Syntheses in the Fatty Series by Means of Aluminium Chloride.

In the laboratory of Friedel a very successful condensation in the fatty series by means of aluminium chloride has lately been carried out by Combes. This chemist observed that acetyl chloride treated with aluminium chloride yields a solid body which contains aluminium. He explains the formation of this compound by the following equation: $6(C_2H_3OCl) + Al_2Cl_6 =$

$$\left(CH_3 - CO - CH_2 - CO - CH_2 - C{\overset{\overset{\displaystyle Cl}{\diagup}}{\underset{\underset{\displaystyle Cl}{\diagdown}}{O}}}\right)_2 Al_2Cl_4 + 4HCl.$$
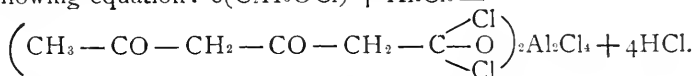
By the action of water the aluminium compound is destroyed and acetyl-acetyl-acetic acid, $CH_3 - CO - CH_2 - CO - CH_2 - COOH$, is set free. The latter, however, decomposes spontaneously into carbonic acid and acetylacetone, $CH_3 - CO - CH_2 - CO - CH_3$.

The mechanism of the reaction between aluminium chloride and acetyl chloride is not fully explained by Combes; the resulting acetylacetone is, however, distinctly characterised as such by a series of reactions. Thus the new compound does not undergo any change when boiled with phosphorus trichloride and acetyl chloride, which demonstrates the absence of hydroxyl. By the action of hydroxylamine and phenylhydrazine, the oximes and a phenylhydrazine compound,

$CH_3 - C(NOH) - CH_2 - CO - CH_3$,
$CH_3 - C(NOH) - CH_2 - C(NOH) - CH_3$,
$CH_3 - C = N - NHC_6H_5 - CH_2 - C = N - NHC_6H_5 - CH_3$
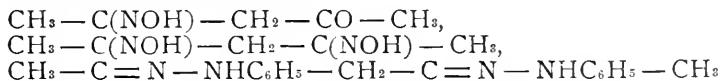
were obtained. These reactions establish without doubt the fact that the new compound is a diacetone. Phosphorus pentachloride changes it into the chloride, $CH_2 = CCl - CH_2 - CCl = CH_2$, which on treatment with alcoholic potash yields the ethyl-ether of a hydrocarbon, $CH \equiv C - CH_2 - C(OC_2H_5) = CH_2$. The hydrocarbon itself, $CH \equiv C - CH_2 - C \equiv CH$, is not stable.

By the action of sodium amalgam in acid solution on acetylacetone, the normal symmetrical bisecondary amylglycol, $CH_3 - CHOH - CH_2 - CHOH - CH_3$, can be easily obtained; and simultaneously the pinacone, $CH_3 - COH - CH_3$

$$\underset{CH_3 - COH - CH_3}{\overset{CH_3 - COH - CH_3}{|}}$$

, and the anhy-

dride of a tetratomic alcohol, which should be called diamyl diglycol, $\quad CH_3 — COH — CH_2 — COH — CH_3$

$$CH_3 — COH — CH_2 — COH — CH_3,$$

$$CH_3 — COH — CH_2 — C — CH_3$$
$$\qquad\qquad\qquad\qquad\quad |{>}O$$
$$CH_3 — COH — CH_2 — C — CH_3,$$
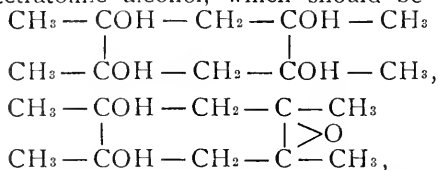
are formed by incomplete reduction of the acetylacetone.

Continued action of chlorine or bromine on acetylacetone produces a hexa-substitution-product as $CCl_3 — CO — CH_2 — CO — CCl_3$. It has been found impossible to substitute by halogens the two hydrogen atoms in the CH_2 group which is between the two CO groups. Those two atoms behave therefore like the hydrogen atoms in the hydroxyls of an acid. They cannot be substituted by the direct action of halogens. By sodium, however, they are very easily replaced ; by the action of alkyl iodides on the sodium compounds thus obtained, sodium can be replaced by alkyls.

Hydriodic acid reacts easily with acetylacetone. By its action on the latter compound, Combes obtained the di-iodo-derivative corresponding to the normal symmetrical bisecondary amylglycol, $CH_3 — CHI — CH_2 — CHI — CH_3$; further, the iodine-derivative of secondary normal amyl alcohol, $CH_3 — CHI — CH_2 — CH_2 — CH_3$, and lastly, normal pentane, $CH_3 — CH_2 — CH_2 — CH_2 — CH_3$. Hitherto it has been very difficult to obtain normal pentane in a state of purity, as it had to be prepared by fractional distillation from American petroleum. The reaction of Combes now makes it possible to prepare this compound on a large scale and in a state of perfect purity.

By treating with alcohol, instead of water, the compound which is formed in the reaction between aluminium chloride and acetyl chloride, Combes obtained the ethyl-ether of acetyl-acetyl-acetic acid, $CH_3 — CO — CH_2 — CO — CH_2 — COOC_2H_5$, and thus proved that his hypothesis regarding the formation of acetylacetone from acetyl-acetyl-acetic acid is correct. Acetyl-acetyl-acetic acid has been characterised as such by the formation of the hydrazine compound. $CH_3 — C(N — NHC_6H_5) — CH_2 — C(N — NHC_6H_5)CH_2 — COOC_2H_5$.

Sodium acts energetically upon acetyl-acetyl-acetic ether, but it has not yet been proved in which CH_2 group substitution by sodium takes place.

Combes has further shown that aluminium chloride reacts in the same way with butyryl, propyryl, isobutyryl and valeryl chloride. Thus this new reaction makes it possible to prepare synthetically a very large number of compounds, which up to date have either been entirely unknown or very difficult and costly to prepare.— (*Ann. chim. phys.*, October, 1887.) E. A. S.

Provisional List of Abbreviations of Titles of Chemical Journals.

The committee of the American Association for the Advancement of Science, known as the Committee on Indexing Chemical Literature, in their last report suggested the following abbreviations of titles of chemical journals. It will be of material assistance, if writers on chemical subjects will generally adopt the suggestions of the Committee. The abbreviations will hereafter be used in this journal:

1. Afh. Fys. Kemi.
2. Agenda chim.
3. Chem. Ztg.
4. Allg. chem. Bibl. (Trommsd.)
5. Allg. J. Chem. Scherer.
   a N. allg. J. Chem. Gehlen.
   b J. für Chem. Gehlen.
   c J. für Chem. Schweigger.
   d J. prakt. Chem.
6. Alm. di chim. agric.
7. Alm. de chim.
8. Alm. Scheid. Apoth.
   a Taschenb. f. Scheid.
9. Am. Chem. J.
10. Am. Chemist.
11. Am. Lab.
12. Analyst.
13. Ann. Chem. (Liebig).
14. Ann. chim. phys.
15. Ann. di chim. (Brugnatelli).
16. Ann. fis. chim.
17. Ann. Chem. Med.
18. Ann. Chem. Phil.
19. [Refer to 14].
20. Ann. Chym. Pract. Pharm.
21. Ann. Pharm. Bastick.
22. Ann. Phil. (Thomson).
23. Annuaire prod. chim.
24. Annuaire chim.
25. Annuaire sci. chim.
26. Annual Rep. Chem.
27. Anno. alm. pei chim.
28. Anno. chim. ital.
29. Anno. scienze chim. nat.
30. Anno. scienze chim. farm.
31. Anti-Adult. Rev.
32. Arch. der Agr.-Chem.
33. Arch. for Pharm. Trier.
34. Arch. ges. Naturl.
35. Arch. für theor. Chem.
36. Arch. thier. Chem.
37. Arsb. Phys. Chemi.
38. Ausw. Abh. Chem. Crell.
39. Ausw. Ann. Chem. Crell.
40. Beitr. Chem. Wasserberg.
41. Beitr. Min. Klaproth.
42. Beitr. Chem. Bucholz.
43. Arch. für physiol. chem.
44. Ber. d. chem. Ges. (*or* Ber.)
45. Berl. Jahrb. Pharm.
46. Bibl. phys. Lit. (Hermbstädt).
    Ann. Chem. Lit.
47. Boston J. Chem.
48. J. de pharm.
49. Bull. math. chim. (Férussac.)
50. Casopis chem.
51. Centrbl. Agr.-Chem.
52. Chem. Gaz.
    Chem. News.
53. Chem. News. Am. Repr.
54. Chem. Record. (Lond.)
55. Chem. Rev. (Lond.)
56. Am. Chem. Rev.
57. Chem. Kal.
    a Techn.-chem. Jahrb.
58. Chem. Ackersmann.
59. Chem. Ann. Crell.
60. Chem. Ind. (Jacobsen.)
61. Chem. phys. oefen.
62. Chem. Archiv Crell.
63. Chem. J. Crell.
64. Chem.-pharm. archief.
65. Chem. techn. Mitthl.
66. Chem. techn. Repert.
67. Chemist. Mongredieu.
68. Chemist. Watt.
69. Chem. and Drug.
70. Chem. Advocate.
71. Chem. and Meteor. J. (Amherst.)
72. Chem. Desk Comp.
73. Chemists' J.
74. Chimiste, Bruxelles.
75. Chimiste, Paris.
76. Compt. rend. *or* C. R.
77. C. R. chim. Montpellier.
78. Crell's Chem. J. Lond.
79. Deutscher Chem. Kal.
80. Edinb. J. Sci.
81. Fortschr. techn. Chem.
82. Fortschr. theor. Chem.
83. Fortschr. Chem. Köln.

84. Gazz. chim. ital.
85. Gazz. chim. techn. (Sembe-nini).
86. Gazz. farm. (Sembenini).
87. Gazz. farm. chim. (Venezia).
88. Giorn. fis-chim. ital.
89. Giorn. chim. veterin.
90. Giorn. farm. chim. (Gajani).
91. Giorn. di farm. Chiappero.
92. Giorn. di farm. Cattaneo.
   a Bibl. di farm.
   b Ann. di farm. appl. (Polli).
93. Giorn. di fis. Majocchi.
94. Giorn. di fis. Brugnatelli.
95. Obs. sur. phys.
   a J. de phys.
96. Jahrb. Erfind.
97. Jahrb. ökon. Chem.
98. Jsb. Agr.-chem. (Ditmer).
99. Jsb. rein. Chem.
100. Jsb. Agr. Chem.
101. Jsb. chem. Techn. (or Wagner's Jsb.)
102. Jsb. phys. Wiss. (or Berzelius' Jsb.)
103. Jsb. Chem.
104. Jsb. thier. Chem.
105. J. chim. phys. Van Mons.
106. J. chim. med.
107. J. chim. Van Mons.
108. J. der Pharm. Trommsd.
109. J. der Phys. Gren.
   a N. J. der Phys. Gren.
   b Ann. der Phys. Gren.
   c Ann. der Phys. Gilbert.
   d Ann. der Phys. Pogg.
   e Ann. der Phys. Wied.
   f Beibl. Ann. der Phys.
110. J. Phys. Krönig.
111. J. techn. Chem.
112. J. Appl. Chem.
113. Nicholson's J.
114. J. Soc. Chem. Ind.
115. K. phys. chem. Abh.
116. Ztschr. Chem.
117. Laboratorium.
118. Laboratory, Boston.
119. Laboratory, Lond.
120. Listy chem.
121. Mag. f. Apoth. (Elwert.)
   a Repert. f. Chem. (Elwert.)
122. Mag. höhere Naturw.
123. Mech. and Chem.
124. Mél. phys. chim.
125. Mem. prat. chim.
126. Mem. Columb. Chem. Soc.
127. Misc. chim. fis. (Pisa.)
128. Mitthl. Chem. (Kletzinsky).

129. Mitthl. Lab. Chem. Brünn.
130. Monatsh. Chem.
131. Monit. prod. chim.
132. Month. Mag. Pharm.
133. Naturh. chem. Notiz.
134. Mag. für Pharm. (Geiger.)
135. Orosi.
136. Penny Mech.
137. Pharm. Times.
   a Chem. Times.
138. Pharm. Centrbl.
   b Chem. Centrbl.
139. Pharmacist.
140. Phil. Mag.
141. Piria.
142. Proc. Am. Chem. Soc.
   a J. Am. Chem. Soc.
143. Proc. Chem. Soc.
   a Q. J. Chem. Soc.
   b J. Chem. Soc.
144. Raccolta fis. chim.
   a Ann. fis. Zantedeschi.
145. [Refer to 37.]
146. Recherches phys.-chim.
147. Recueil trav. chim.
148. Rép. chim. Paris.
149. Rép. chim. pure.
   Rép. chim. appl.
   Bull. Soc. chim. (Paris.)
150. Rép. de pharm. Bruxelles.
151. Rép. de pharm. Paris.
152. Rep. anal. Chem.
153. Rep. chem. Pharm. St. P.
154. Rep. d. Pharm. (Buchner.)
155. Rep. org. Chem. (Löwig.)
156. Rep. Pharm. Russland.
   a Rev. hebd. chim.
157. Rev. Sc. Quesneville.
   a Monit. Sc. Quesneville.
158. Rev. ind. chim.
159. Revista chim.
160. Samml. Abh. Chem. Hoch-heimer.
161. Scheik. bibl.
162. Scheik. bijdr.
163. Scheik. onderzoek.
164. School Mines Q.
165. Taschenb. Scheik.
166. Techn.-chem. Kal.
167. Techn.-chem. Gewerbebl.
168. Techn.-chem. Jahrb.
169. Tekno-kem. J
170. Tidssk. anv. Chemi.
171. Tidssk. Phys. Chemi.
172. Tijdsch. wet. pharm.
173. Toeg. Scheik.
   a Maandbl. toeg. Scheik.
174. N. Gegenst. Chem. (Richter.)

175. Unters. Liebig's Lab.
176. Vjschr. techn. Chem.
177. Yearbook Pharm.
178. Ztschr. anal. Chem.
179. Ztschr. chem. Grossgew.
180. Ztschr. physiol. Chem.
181. Zhurnal Khim.
182. Zpravy Chem.
183. Bull. assoc. chim. France.
184. Bull. Chem. Soc. Washington.
185. Chemiker u. Drogist.
186. Chem.-techn. Centrlanz.
187. Deutsche Chem.-Ztg.
188. J. Anal. Chem.
189. Meddel. Carlsberg Lab.
190. N. Y. Analyst.
  a Am. Analyst.

191. Skand. Kem. Centrlblad.
192. Suppl. enciclop. chim.
193. Tokyo K. Kaishi.
194. Vjschr. Chem. Nahr.
195. Ztschr. Chem. Ind.
196. Ztschr. phys. Chem.
  Am. J. Sci.
  Arch. sc. phys.
  Jen. Ztschr.
  Sitzb. Akad. Berlin.
  Sitzb. Akad. Wien.
  Phil. Trans. Lond.
  Proc. Roy. Soc.
  Proc. Am. Acad.
  Ann. N. Y. Acad. Sci.
  Proc. Acad. Nat. Sci. Phil.

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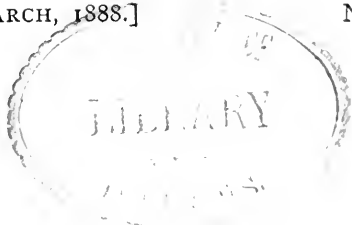
AMERICAN

CHEMICAL JOURNAL.

LIV.—THE RELATIVE VALUES OF THE ATOMIC WEIGHTS OF HYDROGEN AND OXYGEN.[1]

By Josiah Parsons Cooke and Theodore William Richards.

INTRODUCTION.

Since the application by Dalton of the atomic theory to explain the definiteness of the combining proportions of the elementary substances of chemistry, these proportions have been generally regarded as the ratios of the weights of the atoms, and the values assigned to each element have been generally called atomic weights.

The conception was early suggested and advocated by Dr. Prout, an eminent physician of London during the first half of this century, that the elementary atoms were all aggregates of the atom of hydrogen, the lightest atom known. If this were true, it would of course follow that the atomic weights of the elements would all be multiples of the atomic weight of hydrogen ; so that, if the weight of the atom of hydrogen were selected as the unit of the system, all other atomic weights must be multiples of this unit, and therefore whole numbers.

The facts known at the time (1815) were not inconsistent with this view ; but as the methods of chemical analysis were improved,

[1] Proceedings of the American Academy of Arts and Sciences.

and the combining proportions determined with greater accuracy, marked discrepancies from Prout's hypothesis appeared. Still, so great was the hold which the conception had taken upon chemical students, that for a long time the nearest whole numbers to the combining proportions observed were accredited as the true value of the atomic weights, rather than the actual mean of the experimental results ; and this practice is still followed in many standard publications, notably the " Jahresbericht über die Fortschritte der Chemie." In many cases the observed values were so near whole numbers that no important error in the calculation of analyses arose from this practice, the differences neglected being no greater than the uncertainties of analytical method, and this was especially true with regard to the larger atomic weights.

One exception to the theory, however, was so marked that it could not be overlooked, namely, the atomic weight of chlorine, which was capable of being determined with great accuracy ; and all the determinations uniformly gave a result which was closely 35.5. This and a few similar cases suggested the idea that, if the atomic weights were not even multiples of the received hydrogen atom, they might be multiples of the half or quarter hydrogen atom, which would simply amount to taking as the ultimate atom of material things a still smaller unit.

The well known chemist, Dumas of Paris, was led by this view to undertake a redetermination of a large number of atomic weights, and many of the results then obtained are still accepted as authoritative.[1] As was to be expected, Dumas found a much closer agreement with this modified theory than with the original hypothesis of Prout ; but obviously such evidence could have but little bearing on the general theory that the atoms were all aggregates of some common unit, for by taking that unit small enough —even no smaller than the one hundredth of the received hydrogen atom—all the atomic weights, even those most accurately determined, would be expressed by whole numbers within the limits of probable error.

Soon after, Stas of Brussels, a former assistant of Dumas, endeavored to set the question of Prout's theory at rest by an investigation which will be ever memorable for its extreme accuracy.[2] He selected for his investigation those elements whose

[1] Ann. chim. phys., 3d ser. **55**, 129 (1859).
[2] Mémoires de l'Académie Royale de Belgique, **35**. Also Ann. Chem. (Liebig), Suppl. **4,** 168.

combining proportions were capable of being determined with the greatest accuracy, and, working on large quantities of material, with every refinement which a full knowledge of analytical methods could suggest, he obtained results which it seemed impossible to reconcile with the theory in any way. This investigation, published in 1865, seemed at first to disprove the theory altogether.

Nevertheless, when Stas's results came to be collated, and as other determinations of similar accuracy came to be published, the fact appeared that a large number of the most accurately determined atomic weights stood to each other in the relation of whole numbers within the limits of accuracy of the most refined experimental work. The number of these cases was so large that it seemed highly improbable that the coincidences should be the result of chance.

This idea was prominently set forth by Professor Mallet of the University of Virginia, in his admirable paper on the Atomic Weight of Aluminum,[1] which was a striking illustration in point; and the same feature was also made prominent by Professor F. W. Clarke of Washington, after a careful review of all the determinations of atomic weights.[2]

The coincidences appear more striking if the values of the weights referred to are given in values of the oxygen atom assumed to be 16, as has been done by Professor George F. Becker in his digest of atomic weight determinations.[3] The following table from the writer's work on Chemical Philosophy will make clear the point in question.

Atomic Weights most Accurately Determined.

Hydrogen . . . 1.002	Chlorine 35.46
Lithium 7.01	Potassium . . . 39.14
Carbon. 12.00	Calcium 40.00
Nitrogen 14.04	Bromine 79.94
Oxygen 16.00	Silver 107.93
Aluminum . . . 27.02	Antimony . . . 119.92
Sodium 23.05	Iodine 126.85
Magnesium . . . 24.00	Barium 137.14
Phosphorus . . . 31.05	Thallium 204.11
Sulphur 32.07	Lead 206.91

[1] Phil. Trans. 1880, p. 1003.
[2] Smithson. Misc. Coll. ; Constants of Nature, Part V, p. 270.
[3] Ibid. Part IV.

This table includes all the atomic weights which up to 1882 could be regarded as known within one thousandth of their value, and with one or two notable exceptions there is no instance in which the value differs from a whole number by a quantity greater than the possible error, though not always the "probable error," of the processes employed in their determination.

Were these numbers wholly independent of each other and distributed by no law, we should expect to find every possible intermediate value, and the fact that they so nearly approach whole numbers cannot fail to produce on the mind the impression that there is some influence which tends to bring about this result.

It may be that the discrepancies are due to unknown constant errors, which every experimentalist knows are greatly to be feared.   Or it may be that there is in nature a tendency to whole multiples; and this last view, if not compatible with our present conception of the atomic theory, may hereafter appear as one of the phases of a broader philosophy.

The force of evidence which such a distribution of values as the above table presents was brought home to the writer in his investigation of the atomic weight of antimony.[1]   After eliminating various causes of error, he was enabled to determine with great accuracy the atomic weights of antimony, silver, and bromine, in one and the same series of experiments; and it appeared that this ratio was

$$120.00 : 108.00 : 80.00,$$

with a probable error of less than one in the last decimal place. Here then is a ratio of whole numbers within the one hundredth of a single unit.   Since the ratio of the atomic weights of silver and oxygen has been determined with great accuracy, we can extend the above proportion to a fourth term, the atomic weight of oxygen, which appears also as a whole number, perhaps with a somewhat larger probable error.   Still, we have not reached the unit of the system, and when we attempt to extend the ratio to the atomic weight of hydrogen, we find that the most probable value from all experiments hitherto made gives the ratio not of 16 to 1, but of 16 to 1.0025.

If now we wished to refer to the hydrogen unit the atomic weights of antimony, silver, bromine, and oxygen, whose ratios of

[1] Additional Experiments on the Atomic Weight of Antimony, Am. Acad. Proc. **17**, p. 13, by Josiah Parsons Cooke.

whole numbers had been determined as above, it was only neces-
sary to divide all the terms of the above proportion by 1.0031,
when we obtain the series of values given below the others, and all
semblance to the hypothesis of Prout disappears, although of
course the second series of numbers bear the same ratios to each
other as the first:

Antimony.	Silver.	Bromine.	Oxygen.	Hydrogen.
120.00	108.00	80.00	16.01	1.0031
119.60	107.66	79.75	15.96	1.00

The numbers in the lower of the two proportions appear as
uncommensurable as Stas maintained that they were, and the same
is true of most of the atomic weights, when given, as is usual in
recent text-books, on the basis of the hydrogen unit.

When as the result of his investigation on the atomic weight of
antimony there was presented to the writer the ratios of whole
numbers as shown in the first of the above proportions, with the
single exception of the atomic weight of hydrogen, the question was
at once suggested : Is the ratio of the atomic weights of oxygen and
hydrogen in fact that of 16 : 1.0025, as the general average of all trust-
worthy determinations hitherto made seems to indicate, or was there
some constant error lurking in these results which caused the very
slight variation from 16 to 1 required by the theory?   In looking
at the proportion thus displayed, it seemed as if the variation from
the theory must be apparent, and he determined to ferret out the
hidden error if possible.   This investigation was undertaken in the
autumn of 1883, but owing to the condition of the writer's sight
the work has been greatly delayed.

No one can study the record of the investigations by which the
ratio of the weights of the oxygen and hydrogen atoms has been
determined, without receiving the impression that they are by no
means decisive in regard to the theory we are discussing, and it
is also equally evident that this ratio, if it could be fixed beyond
doubt, would be a crucial test of the theory.

Previous Work.

The methods by which the atomic weights of oxygen and hydro-
gen have been determined may be divided into two classes : first,
the direct method of determining the ratio in which the proportions
of oxygen and hydrogen uniting to form water were actually

weighed ; secondly, the confirmatory method, to whose results small weight could be given independent of the first.

Among confirmatory methods we must unquestionably class the classical determinations by Regnault of the density of oxygen and hydrogen gases under normal conditions at Paris ; that is, in so far as these determinations bear on the question of the ratio of the atomic weights.

According to the molecular theory the ratio of the densities of oxygen and hydrogen gases could only be the ratio of their molecular or of their atomic weights when both materials were in the condition of perfect gases, of which condition the test would be an exact conformity to Mariotte's law. Now, as Regnault himself elegantly demonstrated, oxygen and hydrogen gases at the standard conditions of temperature and pressure not only do not exactly obey Mariotte's law, but the deviations from the law in these two cases are in the opposite directions, oxygen gas being condensed by increasing pressure more, and hydrogen gas less, than the law requires. Hence theory would not lead us to expect that the ratio of the densities of these gases at the standard conditions would be the exact ratio of their atomic weights. But obviously it may be that this inference from the molecular theory is not legitimate, or it may be that the effect of the imperfect aeriform condition would not perceptibly influence the apparent atomic ratio ; and hence the confirmation afforded by Regnault's results is of value.

In t he same category we must class also the determination of the atomic weight of oxygen made by Thomsen of Copenhagen, who weighed the amount of water obtained by burning a measured volume of hydrogen gas. Here the reduction of the volume to weight involved a knowledge of values and conditions which could not be known with the greatest accuracy, and unfortunately the details of the experiments have not been published.

Again, we should class simply as confirmatory results deduced indirectly, and involving the values of other atomic weights, however accurately these subsidiary values may be supposed to be known ; such, for example, as Stas's determination of the amount of chlorine in ammonic chloride.

Turning now to the actual direct determinations of the combining proportions of oxygen and hydrogen, there are only two which are of any present value. Of these by far the most important is the classical investigation of Dumas, " Researches on the Composition

of Water."[1] This is one of the most memorable investigations in the history of chemistry, and its general principles are known to every student of the science. An indefinite amount of hydrogen was burnt by means of cupric oxide; the amount of oxygen consumed was determined by the loss of weight of the combustion tube, and the amount of water formed was collected and weighed directly. The experiments were on a very large scale, the amount of water produced varying from 15 to 70 grams. The greatest care was taken to insure the purity of the materials used, every known experimental means was employed to secure accuracy, and all necessary corrections were applied to the results. Estimated on the system at present in use, the value of the atomic weight of oxygen obtained by Dumas as the mean of nineteen determinations was 15.9607, with a probable error of $\pm$0.0070, the highest value being 16.024, and the lowest 15.892.

The investigation of Erdmann and Marchand[2] was far less extended, and some of the precautions taken by Dumas were neglected because deemed unnecessary. No pains seem to have been taken to obtain pure cupric oxide, and the material used in several of the determinations was described as " kaufliche Kupferglühspan," while that used in the others was obtained by igniting cupric nitrate ; and no proof is adduced in either case of the purity of the material employed.

The results are divided into two groups, and in the experiments of the second group the air was exhausted from the combustion tube before weighing ; but it appears from the paper that the marked difference between the two series of experiments depended rather on the character of the cupric oxide, and on varying conditions used, than on this circumstance. The first series of four results, when averaged, gave the value 15.937, with a probable error of $\pm$ 0.0138, while the mean of the second series was 16.009, with a probable error of $\pm$ 0.0030. The study of the paper, however, does not confirm the expectation that the results of the second series are more trustworthy ; for the closer agreement and smaller probable error appear to be the result of the identity of conditions, which was maintained in this series, but not in the first. Judging from the paper, we should be inclined to place most reliance on the first series, in which the conditions of the experiments were varied, rather than on the second, which seems obviously to be influenced by some constant error.

[1] Ann. chim. phys., 3d ser. **8**, 189 (1842).   [2] J. prakt. Chem. 1842, **26**, 461.

The results, then, thus far obtained, are as follows :

Direct Determinations.

Dumas (nineteen determinations)   15.9607 ± 0.0070
Erdmann and Marchand (first four)   15.9369 ± 0.0138
    "   "   " (second four) 16.0095 ± 0.0030

Confirmatory Determinations.

Dumas and Boussingalt[1] (gas densities)   15.954 ± 0.031
Regnault[2] (gas densities)   15.961 ± 0.0044
Thomsen[3] (not fully described)   15.960

The one process by which the relative combining proportions of oxygen and hydrogen have been hitherto directly determined is open to serious criticism.   In the first place, the circumstance that the weight of the hydrogen is eight times smaller than that of the oxygen, and that this weight has only been estimated by difference, is exceedingly unfavorable to the accuracy of the process. It can easily be seen that, in order to establish a ratio like 1 to 8, the highest accuracy demands that each term of the proportion should be known to an equal degree of exactness.   Thus if in a given experiment we have 8 grams of oxygen uniting with 1 gram of hydrogen, it is of no avail to weigh the oxygen to the tenth of a milligram, unless we can weigh the hydrogen to the same proportionate degree of accuracy.   For an error of eight tenths of a milligram in the weight of the oxygen, or an error of nine tenths of a milligram in the weight of the water, will have no more influence on the ratio we are seeking than an error of one tenth of a milligram in the weight of the hydrogen.   Now, in the process we are discussing the weight of the water can be determined to within a few tenths of a milligram ; that is, with all the accuracy with which our problem requires that the larger term of the proportion 8 to 1 should be known.   It is quite different with the weight of the oxygen.   This last is found by weighing the glass combustion tube containing cupric oxide before and after the experiment, and between the two weighings the tube is heated to a low red heat for several hours while a stream of hydrogen gas is passing through it ; and there are several causes which may lead

[1] Compt. rend. **12**, 1005 ; also Constants of Nature, Part V, p. 6.
[2] Compt. rend. **20**, 975 ; also Constants of Nature, Part V, p. 6.
[3] Ber. d. chem. Ges. **3** (1870), 928 ; also Constants of Nature, Part V, p. 8.

to the variation of these weights, independent of the oxygen which has been used up in the process. We shall allude to some of these causes below, but their effect would be comparatively unimportant if they only led to a small error in the observed weight of the oxygen. Unfortunately their effect is not thus limited ; for when, in order to find the weight of the hydrogen, we subtract from the weight of the water, which may be regarded relatively as accurately known, the weight of the oxygen, which may be for the causes referred to slightly erroneous, the whole error appears in the weight of the hydrogen thus found, and in the opposite direction. If, for example, the weight of the oxygen is too large, the weight of the hydrogen will be too small by exactly the same amount ; and although the error may be an inconsiderable part of the weight of the oxygen, it may be a very appreciable quantity in the weight of the hydrogen.

On the other hand, if a means could be devised for weighing the hydrogen, leaving the oxygen to be determined by subtracting this smaller weight from the weight of the water, then a small error in the observed weight of the hydrogen would have no appreciable effect on the weight of the oxygen.

Dumas fully recognised the source of error to which we have referred, and in his paper on the subject wrote what may be translated as follows :

"Of all analyses presented to a chemist, that of water is the one which offers the greatest uncertainty. Indeed, one part of hydrogen unites with eight parts of oxygen to form water, and nothing would be more exact than the analysis of water if we could weigh the hydrogen as well as the water which results from its combustion. But the experiment is not possible under this form. We are obliged to weigh the water formed, and the oxygen which was consumed in producing it, and to determine by difference the weight of the hydrogen which has entered into combination. Thus an error of $\frac{1}{900}$ in the weight of the water, or of $\frac{1}{800}$ in the weight of the oxygen, is equivalent to an error of $\frac{1}{80}$ or $\frac{1}{90}$ in the weight of the hydrogen. Let these two errors be in the same direction and the total error will amount to $\frac{1}{40}$."

In the second place, however carefully the exterior surface of the combustion tube may be guarded, it is impossible that the contents of the tube should bear the same relations to the surrounding atmosphere before and after the combustion. We begin with a tube

containing cupric oxide in different states, and we end with it containing reduced copper, whose condition will vary more or less with the character of the oxide employed ; and the power of these materials to occlude air or hydrogen is an unknown quantity in our experiment. That it is an appreciable quantity is evident from several incidental observations.

Dumas endeavored to avoid any source of error arising from this cause by exhausting the combustion tube before weighing it, but he himself expresses a doubt whether a trace of hydrogen might not have been left. Erdmann and Marchand in part of their experiments resorted to the same expedient, but their results obviously vary with the condition of the cupric oxide employed; and the following remarks of Schutzenberger, in a discussion of the variability of the law of definite proportions before the Chemical Society of Paris in 1883, as quoted in the " American Journal of Science," 3d series, Vol. XXVI, page 65, have an important bearing on the same point :

" When water is synthesised by reduction of a known weight of CuO, by weighing the reduced Cu and the water formed, it is found that the ratio of O to H is not constant, but varies with the state of division and of saturation of the oxide, the duration of contact of the water formed with the oxide, and with the temperature, from 7.95 to 8.15. The latter value is obtained with a saturated and divided oxide filling the tube, the former with oxide in lumps filling the tube for a space of 25 cm. With a larger empty space the ratio has fallen to 7.90. When the synthesis of water is effected by weighing the hydrogen consumed (as by dissolving a known weight of zinc in HCl) and the water formed, the ratio differs according to the contents of the combustion tubes. If it contains granular CuO of a length of 80 cm. heated to redness, the ratio O : H is 7.96 to 7.98 to 1 ; at a low temperature, 7.90 to 7.93 ; if the CuO is replaced by $PbCrO_4$, from 7.89 to 7.93."

In addition to all this, impurities in the oxide of copper might have a serious influence on the result. As before said, Erdmann and Marchand speak of using "kaufliche Kupferglühspan "; but in our work we could find no commercial cupric oxide which did not contain a marked amount of arsenic. We examined a number of specimens coming from the best German and American dealers, and there was not a single instance in which we did not find arsenic, and even when the material was marked " purissimum." In some

cases the amount of arsenic was so great that, after successive reductions and oxidations, abundant crystals of arsenious oxide collected at the exit end of the combustion tube. It is unnecessary to add that the hydrogen used was free from all such impurity.

For our own experiments, of which the results are given below, not only was the oxide of copper prepared from absolutely pure electrolytic copper, but also, as will be shown, the combustion tube was left at the end of the determination as it was at first, and the same tube was used for a number of experiments.

Apparatus for weighing Hydrogen.

In entering on a new investigation of the oxygen and hydrogen ratio, it was evident at the outset that no advantage was to be gained by multiplying determinations by the old method. The only hope of improvement lay in finding some method of weighing the hydrogen with sufficient accuracy; and it was essential to determine this weight to within one ten-thousandth, or at least one five-thousandth, of its value.

A gas can only be weighed by enclosing it in a glass globe, or some similar receiver, and hydrogen is so exceedingly light that its total weight can only be a very small fraction of the weight of the containing vessel. Moreover, as the buoyancy of the air is fourteen and one half times as great as the weight of the hydrogen, the variations in buoyancy caused by changing atmospheric conditions have an all-important effect on the apparent weight. The late Professor Regnault, of Paris, devised, however, a very ingenious method of compensation, which could readily be applied in this case. It consisted in balancing the globe containing hydrogen, hung to one arm of the balance, by a second globe of exactly the same external volume and made of the same material, hung to the opposite arm; and so arranging the balance case that they should hang in the same enclosure, and therefore be equally affected by atmospheric changes. This method was applied in the problem before us; and after a number of trials it was found possible to make the compensation so accurate that under good conditions the weight of a globe holding five litres of gas did not vary more than one tenth of a milligram through large changes of temperature and pressure. In order now to weigh hydrogen with this apparatus, it was only necessary to exhaust the air from the glass receiver, and, after balancing it as described, to fill it with

pure gas, when the increased weight—less than half a gram with our apparatus—was the weight of hydrogen required.

The balance employed was an excellent one, made about twenty years ago by Becker and Sons, of New York. With a load of five hundred grams in each pan, it turns very perceptibly with one tenth of a milligram, and shows this small difference of weight with very great constancy.

The globe and its counterpoise were hung from hooks soldered to the bottoms of the pans by means of wires which swung freely through small holes made for the purpose through the bottom of the balance case, and also through the top of the shelf on which the case stood. The enclosure in which the globe and its counterpoise hung was à box made of tinned iron fastened to the bottom of the shelf, and having doors in front like an oven, through which the globe could be removed or hung in position. This case was coated with lampblack on the inside, in order to secure uniformity of temperature ; and the air was kept dry by means of two large dishes of sulphuric acid, placed on shelves at the top of the case. We first placed the sulphuric acid dishes on the bottom of the case in the usual way, but we found it impossible thus to secure a uniform condition of the atmosphere within ; and as moist air is necessarily lighter than an equal volume of dry air at the same temperature and pressure, it is obvious that any drying material will have the greatest efficiency when placed near the top of the space to be protected. The tin box was itself enclosed in a cupboard, but not otherwise protected ; and the balance case was surrounded by curtains, in order to shield the beam from radiation.

With the apparatus so arranged, it was found possible to obtain most satisfactory and concordant results to tenths of a milligram when the change in the temperature of the balance-room was not very rapid ; but any sudden changes produced by artificial heating would cause slight currents of air in the interior of the case, whose effect became very sensible, but whose influence we were able to eliminate. The best series of results, however (the second series in the table below), was obtained during the month of June, when there was no artificial heat in the building, and the temperature varied but little during day and night.

The globe used for holding the hydrogen—shown in Fig. 1 in about one sixth of its actual dimensions—has an interior capacity of 4961.5 cubic centimetres, and weighs 570.5 grams. The cap with
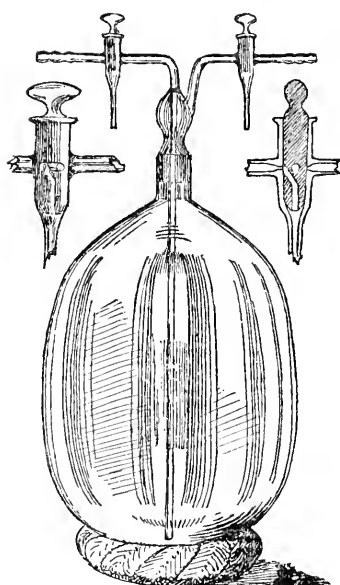
FIG. 1.

the connecting tubes was ground into the neck, and this joint, as also the stopcocks, was so carefully made that there was absolutely no leakage, and the globe would hold a vacuum indefinitely; as was shown frequently by its remaining hung on the balance for weeks together when exhausted without change of weight. The apparatus was made by Emil Greiner, of 79 Nassau Street, New York, whose careful workmanship greatly contributed to the success of our investigation. The details of the stopcock are shown at the sides; and it will be noticed that, besides the direct way, there is a side way through the plug of the stopcock independent of the first, by which, when the stopcock is closed, a connection is established with the base of the cock, through which the gas may escape.

Assume now that the interior of the globe has been exhausted, and a gas current established through this side aperture from one of the generators employed. On turning the stopcock, the side aperture is first closed, and then the direct way slightly opened, so that all the gas evolved now passes into the globe; and it was found possible to regulate the current with such nicety as not to cause any sudden changes of tension in the generator, which was always provided with an overflow by means of which the tension could be watched, and according to which the stopcock was regulated.

The filling of the globe was one of the critical points of the determination. It generally occupied from one to two hours, and during all this time it was necessary, with the hand on the stopcock, carefully to watch the tension at the overflow already mentioned, and represented in Fig. 5, and Figs. 7 and 8 of Plate. From the beginning to the end of the operation there was a greater tension in the generator than in the outside air, by about

one inch of mercury. When the connection was once established between the generator and the globe, there was absolutely no leakage through the side way, as was tested in several cases by dipping the mouth of the tube at the base of the cock under mercury.

The whole process of weighing the hydrogen was finally reduced to the following manipulation. The globe was connected by means of a rubber hose with a rotary air-pump having automatic valves, made by E. S. Ritchie, of Boston. It was then exhausted to within 1 mm. of mercury. Next, closing the cock and disconnecting the globe, it was cleaned with distilled water and fine cotton cloth; at least, this was done five or six times during the determinations. But as the globe when out of the balance case was always protected by a cylindrical tin box with a cover, from which the exit tubes projected, it was usually only necessary to clean the exit tubes in this careful manner, simply dusting off the globe with a large camel's-hair brush, before hanging it in the balance case. In this part of the operation it was necessary to take care not to communicate to the globe a charge of electricity by rubbing it with a perfectly dry cloth.

The globe was hung on a wire stirrup, which caught the exit tubes, as the glass joint was sufficiently strong to support the weight of the globe. The globe was so nearly balanced by its equipoise that when exhausted it only required about one decigram to establish equilibrium. The time required to attain perfect equilibrium varied with the conditions. If the glass had been previously cleaned as described above, perfect equilibrium might not be reached for forty-eight hours, or even longer, while, if the glass had only been dusted, twelve hours were generally sufficient.

After the tare had thus been taken, the globe was removed from the balance, placed in the protecting case, and filled with hydrogen as just described. The inlet tube, to which a rubber connector had been attached, was scrupulously cleaned as before, and the globe was again dusted and hung on the balance. During all these transfers the globe was always handled with clean cotton cloth, and the hands never came in contact with the glass. The increased weight was now the weight of the hydrogen; and as the volumes equipoised were exactly the same, and the additional weight was represented by less than five tenths of a gram of platinum, any correction for the buoyancy of the atmosphere is unessential.

Combustion Apparatus.

The apparatus by which the combustion of the hydrogen was made is represented in the Plate accompanying the paper (Fig. 6). It is made up of a series of small combustion furnaces, which are a modification of a kerosene-oil stove called "the American," very much used in the United States. This stove, as adapted to chemical uses by the writer, is shown in Figs. 2 and 3, and it has proved of great value, not only for elementary chemical experiments in school courses, where illuminating gas is not to be had, but also in a well equipped chemical laboratory. The stove is made for burning kerosene oil, but alcohol can also be burnt in it with decided advantage for chemical work. The figure of the stove has been drawn to about one sixth of the actual size.
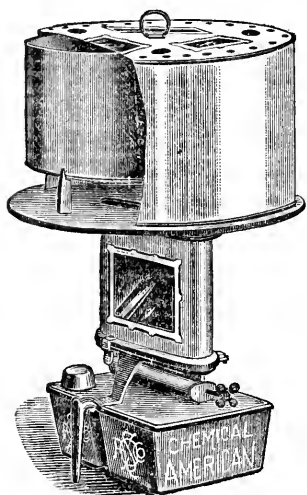
In the figure of the combustion apparatus (Fig. 6, Plate) it will be noticed that the globe, protected by its case, stands about in the middle of the line. By means of a suction pump attached to the extreme right of the apparatus, a current of air is maintained through the whole length. Beginning now at the extreme left, the air first passes over reduced copper and is deprived of its

Fig. 2.
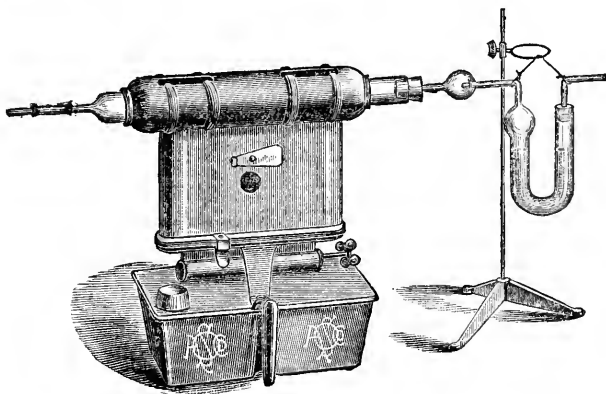
Fig. 3.

oxygen. It next passes over cupric oxide, by which any traces of hydrogen that had remained occluded by the reduced copper, or any traces of hydrocarbons in the air itself, are burnt. It next passes through caustic potash bulbs, and then through a system of driers, meeting successively calcic chloride, sulphuric acid, and phosphoric pentoxide. It now enters the globe through the inlet tube reaching to the bottom, carrying before it the hydrogen into the combustion furnace.

The water from the combustion was collected in a condenser—the details of whose construction are represented in Fig. 4—which was shielded from the furnace by a screen of asbestos paper. Nine tenths of the water was condensed in the middle tube, and all but the last traces of the aqueous vapor were absorbed by the sulphuric acid through which the air subsequently bubbled up at the bend of the U tube, between glass beads, which broke the ascent and divided the bubbles. With this condenser was connected a U tube containing phosphoric pentoxide, which absorbed the last traces of the aqueous vapor, seldom, however, gaining in weight more than two milligrams during a combustion lasting from seven to eight hours. Then follows a safety tube containing calcic chloride (or in some cases phosphoric pentoxide), to prevent any reflex diffu-

Fig. 4.

sion, and finally, an adaptation of the principle of Mariotte's flask to regulate the velocity of the air current. It will be seen that the open mouth of the central tube of this last apparatus dips under the mercury in the tall jar, so that by raising or lowering it the strength of the current could be exactly regulated.
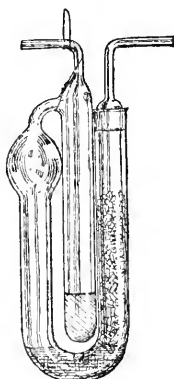
Before beginning a combustion, the place of the hydrogen globe was supplied by a straight piece of glass tubing, and the air current maintained through the heated combustion tube until the cupric oxide was perfectly dry. Next the furnace at the extreme left was lighted, and the current continued until the oxygen in the air of the drying tubes had been so far replaced by nitrogen as to remove all risk of subsequent explosion.

Meanwhile the globe and condensing tubes were made ready, and first the globe and next the condensing tubes were placed in position, all the rubber connectors required having been previously

dried in the current of dry air, and the joints were so contrived that subsequently the stream of gas came in contact with the smallest possible surface of the rubber connectors. The combustion lasted, as has been already stated, from seven to eight hours, and during this time quite a rapid current of air was drawn through the apparatus.

Our preliminary experiments plainly showed that the rapidity of the current within practicable limits had no appreciable effect on our results, and this is due to the fact that the current entered the globe and left the condensers under precisely the same conditions. More than nine tenths of the water was condensed during the first half hour, the drops falling regularly from the mouth of the inlet tube, and after two hours all traces of cloudiness disappeared from this tube or its connections, showing that the air coming over was perfectly dry. The water thus collected was absolutely clear and limpid.

After the first hour the combustion furnace used for removing oxygen from the air, at the extreme left, was taken away, and by the end of the combustion the reduced copper in the combustion tube proper was again completely oxidised, leaving the globe and all the tubes filled with normal air, as at the beginning of the process. It only remained now to remove the condensers and reweigh them with all necessary precautions. At both weighings the barometer and thermometer were observed, and the small, usually insignificant correction for buoyancy caused by a change in the atmosphere during the interval was carefully estimated.

The question of the time of running the combustion after the production of water had sensibly ceased was one that was carefully considered. The time mentioned above—eight hours—was far outside the necessary limits, and was reached only after a large number of experiments. That a very long continuance of the current after the combustion was practically ended was unnecessary was clearly shown by several circumstances. In the first place, the duration of the combustion beyond the limit we have named made no difference in our results, as was repeatedly shown. Again, in one instance, after detaching the condensation tubes and weighing them, they were again put in place and the combustion continued three hours longer, during which time the tubes gained no appreciable weight. In another instance, when a suspicion arose that possibly some hydrogen might be occluded on the walls

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of the globe, the condensation tubes having been dismounted and weighed as before, the globe was also dismounted and heated over the free flame of a Bunsen lamp to as high a temperature as the glass would safely bear, over 300° C., and then, the apparatus having been remounted, the combustion was continued for one hour. Here again the condensation tubes gained only a small fraction of a milligram in weight, an effect which might easily be accidental, and which was wholly without influence on the result.

Apparatus for preparing Hydrogen.

In the preliminary determinations the hydrogen was drawn from a large copper generator charged with zinc and dilute sulphuric acid. The zinc and sulphuric acid were wholly free from arsenic, and of the best quality, but not absolutely pure ; and the writer depended upon an elaborate system of washers and driers for purifying and drying the gas. He found the greatest difficulty in removing the last traces of sulphurous oxide, which hydrogen prepared in this way always carries. The presence of this trace cannot be detected by litmus paper, but is immediately indicated by the production of hydric sulphide when the gas is passed over heated platinum sponge; and by interposing a tube containing platinum sponge maintained at a low red heat, followed by a set of potash bulbs, this impurity can be entirely removed. It can also be removed by washing with a strong solution of potassic hydrate alone, if the gas remains long enough in contact with the solution. It was found, however, that a series of potash bulbs was insufficient for this purpose ; but two of the long washers represented in the background of Fig. 5 and in Figs. 7 and 8 (Plate), where the gas in small bubbles travels up a tube $5\frac{1}{2}$ feet long, are sufficient to remove the sulphurous oxide from even a quite rapid current of hydrogen gas. A series of preliminary determinations was made with hydrogen gas thus prepared and purified, and it was obvious from an inspection of the results, as well as from the difficulties which were experienced in keeping all the joints of this complicated apparatus tight, that the irregularities arose from the diffusion of the air into the hydrogen at some one or other of these joints. It was therefore next sought to simplify the apparatus, and to depend upon the purity of materials rather than on the completeness of purifying methods for obtaining pure hydrogen. Meanwhile, for reasons stated below, the writer had reduced very
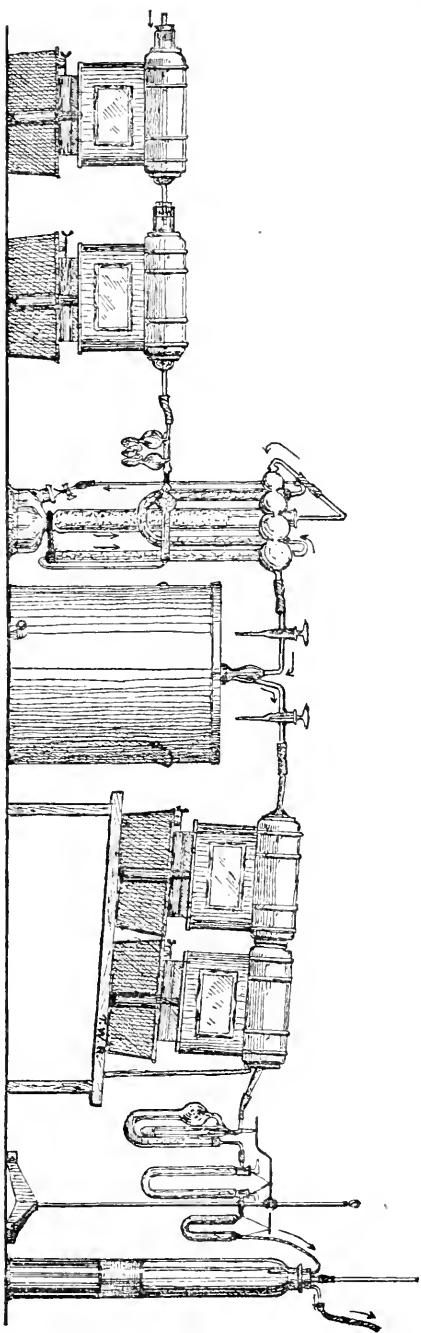
Fig. 7.

Fig. 8.

Fig. 6.
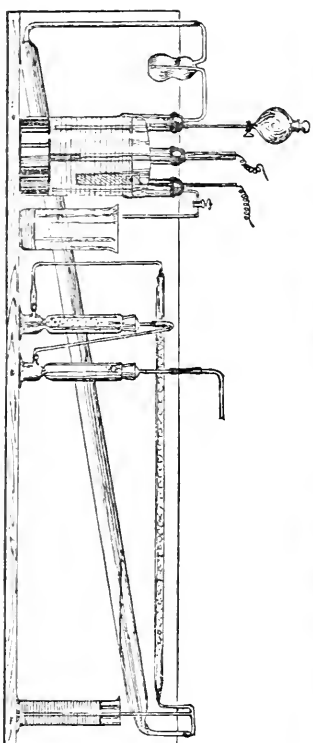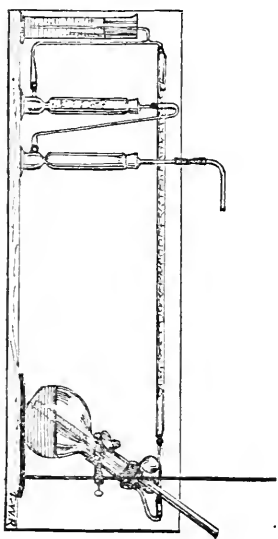
materially the scale of his operations, and this rendered unnecessary the large generator we had first employed.

The second apparatus that was constructed is represented in Fig. 5. Of this, the generator, in which hydrogen is made from pure zinc and hydrochloric acid, is the same as that described by Julius Thomsen.[1] The Wolff bottle is filled with pure granulated zinc, and the upper bottle contains pure hydrochloric acid diluted about one half. By means of a glass stopcock the acid is allowed to flow into the zinc drop by drop, and in this way the current of
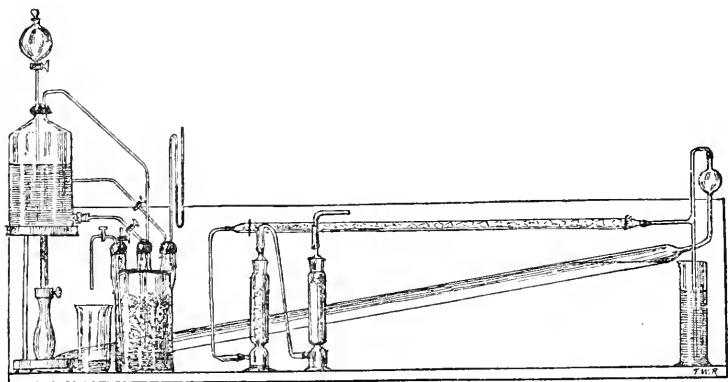
Fig. 5.

hydrogen can be quite closely regulated. Tubes protected by stopcocks are provided for adding fresh charges of acid and for drawing off the solution of zinc chloride; also a tube connecting the upper part of the two bottles enables the operator to effect these transfers without introducing any air. The gas from this generator passed first through a long potash tube inclined at about 10° to the horizon, then through a tube about three feet long filled with calcic chloride, then through a glass tower filled with glass beads drenched with sulphuric acid, and lastly through a second tower filled with phosphoric pentoxide. As many of the joints as possible were made by fusing together the glass, and all the others were protected by a cement consisting of equal parts of pitch and gutta-percha. It will be noticed that an overflow is provided at the point where the potash tube connects with the calcic chloride tube, the open mouth of the overflow tube dipping about six or eight inches deep under concentrated sulphuric acid. This over-

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[1] Thermochem. Untersuch. **1**, 28.

flow indicated the least change of tension of the hydrogen in the apparatus, and would have shown the least leak if it had existed ; but the apparatus as thus constructed remained absolutely tight so long as it was in use.

With the hydrogen drawn from this apparatus, the first determinations were not wholly satisfactory, and the cause of error was traced to the air dissolved in the dilute hydrochloric acid with which the generator was charged. In all the succeeding determinations the greatest pains was taken to remove the last traces of air by boiling the dilute acid and allowing it to cool in a stream of hydrogen ; and as additional precaution, while the solution was still warm, the gas was exhausted from the containing vessel and pure hydrogen run in, several times in succession, the pure acid being finally conveyed into the generator entirely out of contact with the air. The need of all these precautions will be seen when it is considered how small an admixture of air or of nitrogen will materially influence the weight of the hydrogen. If only one ten-thousandth of the volume of the hydrogen were replaced by air during the process of filling the globe, this would cause an apparent increase of weight in the hydrogen of five tenths of a milligram, and that, other things being equal, would reduce the atomic weight of oxygen two hundredths of a unit.

The precautions used in filling the globe have already been described in detail, and with hydrogen from the apparatus, constructed and charged as just described, were made the five consecutive determinations whose results are given as of the first series in the table on page 107. These, and all the determinations given in the table, were made by the writer's pupil and assistant, Mr. Theodore William Richards, to whose experimental skill the success of the investigation is largely due, and without whose assistance the work could not have been completed in the present condition of the writer's sight. The mean of these first five results, as will be noticed, is but little less than that obtained by Dumas, and the probable error, $\pm$ 0.0048, is considerably less than that of Dumas. In order to understand how this result appeared to the writer, it must be remembered that he started with a certain prepossession in favor of the hypothesis of Prout, based on his previous work on antimony ; and, furthermore, that the effect of the causes of error which had been encountered and overcome all tended to lower the atomic weight ; and the result obtained was a maximum which had

been reached after every known precaution had been taken. But although this maximum was essentially the same as that obtained by Dumas by an obviously less direct and less accurate method, yet it was still possible that there might be some constant error, and that some cause might yet be found which would raise the maximum by the forty-six thousandths required to give the whole number 16.   It was true that the probable error was only about one tenth of this difference; still, as the materials had been purified, the maximum had constantly risen, and the theoretical limit was in sight.   In reviewing the work, it was obvious that the degree of accuracy of the methods used for determining the weights both of the hydrogen and of the water was so great that no possible error in these values could account for the difference in question.   This would imply an error of 1.2 milligrams in the weight of the hydrogen, and of 10.8 milligrams in the weight of the water, and the possible error of a single determination—leaving out of account the reduced probable error of the average value— was far within these limits.   If there was a constant error, it must result from the want of purity of the hydrogen gas, and we therefore determined to try another method for preparing the hydrogen.

The apparatus next used is represented in Fig. 7 (Plate), and differs from the last only in the generator.   Here the generator is a three-necked bottle having a capacity of about two litres, filled to about one eighth of its capacity with a semi-fluid amalgam of mercury and pure zinc.   On this rests dilute hydrochloric acid, containing about twenty per cent. of HCl, nearly filling the bottle. Into this acid dips a platinum electrode, while a straight glass tube passing through the middle neck and dipping under the amalgam gives the means of establishing an electrical connection between the large platinum plate which forms the negative electrode and the amalgam.   In addition, a siphon tube for drawing off the acid when saturated with zinc, a funnel tube for introducing a fresh charge, and an exit tube, all well cemented to the several necks of the bottle, complete the generator.   When the electrical connection is broken, all chemical action ceases, but on connecting by a wire the platinum electrode with the amalgam, a very steady but slow evolution of hydrogen gas takes place, which can be regulated with the greatest nicety by varying the resistance of the connecting wire.   On interposing two cells of a Bunsen battery the evolution of gas becomes very rapid.   Besides its special use in this connection, the apparatus will be found of great value as

giving an absolutely constant source of pure hydrogen whenever required. In charging the generator with acid the same care was taken to exclude every trace of air as with the previous apparatus, and with hydrogen thus prepared a second series of five consecutive determinations was made, whose results are given in the table on page 107, below those of the first series; and it will be noticed that, while the average value obtained is essentially identical with the previous result, the agreement of the several determinations is more close, and in consequence the probable error is reduced more than one half. A closer agreement under the circumstances could not possibly be expected.

Such a striking confirmation of the previous result seemed very conclusive, and the very small probable error indicated a command of the method which was very satisfactory. Still, it could not be proved that there might not be a constant impurity in the hydrogen used. As the hydrogen had passed every possible chemical test unimpeached, the only possible impurity that could be suspected was nitrogen, and Mr. Richards therefore made a careful spectroscopic examination, searching for the more conspicuous nitrogen lines in the spectrum obtained by passing an induction current through a rarefied atmosphere of the gas from the generator just described; but not the faintest trace of any of these lines could be seen.

Still, as in the electrolytic method of preparing the hydrogen the same materials, hydrochloric acid and zinc, were used as in the first series of experiments, it was determined to procure hydrogen by a wholly different chemical process, using the well known reaction of metallic aluminum upon a solution of potassic hydrate.

The purest aluminum sheet that could be obtained in the American market was procured for the purpose, and the apparatus represented in Fig. 8 (Plate) was used for generating the gas. The generator here was a simple flask holding a strong solution of chemically pure potassic hydrate, and the aluminum was introduced in small pieces through a large open tube—dipping under the surface of the solution—the liquid being maintained at a level near the open mouth of the tube by the tension in the interior of the apparatus. The small strips of aluminum were carefully cleaned, and caused slowly to slide down the tube; the evolution of hydrogen from the surface began as soon as the strips of metal touched the liquid, and became very active in the tube before they dropped into the flask. And this action insured the removal of any traces

of air which might adhere to the surface. In this apparatus the long caustic potash washer was not used, as being no longer necessary, and the gas was passed through caustic potash bulbs to remove the spray, and then through a calcic chloride tube, and over sulphuric acid and phosphoric pentoxide, as before.

With hydrogen thus prepared, the six determinations of the third series in the table were made; and it will be seen that the average of the results is a value which is essentially identical with the average values from the other two series. The probable error in this last series is larger than in the second, although still very small; but the difference is due, as the note-books plainly show, to the different conditions under which the two series were made. As before stated, the compensation of the balance was perfect, and the apparent weight of the globe did not alter by a tenth of a milligram, even with wide variations of temperature and pressure, so soon as those changes became constant. But when the changes of temperature in the balance-room were rapid, currents of air were established in the case, however great care was taken in protecting it, which rendered the apparent weight irregular to the extent of one or two tenths of a milligram; and the third series was made under less favorable conditions in this respect than the second. This point is illustrated by the following notes of two determinations, which are given in full, in order that all the circumstances connected with the determinations may be seen.

SERIES II. *Determination 5.*

Weighings of the globe :   Grams.

Exhausted.	June 6th,	6.00 P. M.	Tare $=$ 0.1960
	7th,	7.25 A. M.	$=$ 0.2011
	"	8.30 A. M.	$=$ 0.2011
	"	11.20 A. M.	$=$ 0.2011
	"	2.00 P. M.	$=$ 0.2011

                                                          0.2011

Filled with Hydrogen.	June 7th,	7.20 P. M.	Tare $=$ 0.6100
	8th,	8.00 A. M.	$=$ 0.6156
	"	10.00 A. M.	$=$ 0.6156
	"	12.15 P. M.	$=$ 0.6154
	"	7.50 A. M.	$=$ 0.6155
	"	9.30 A. M.	$=$ 0.6155
	"	11.40 A. M.	$=$ 0.6155

                                                          0.6155

Weight of Hydrogen taken $= 0.6155 - 0.2011 = 0.4144$ gram.
The combustion was started at 11 A. M. and stopped at 6 P. M.

Weight of P_2O_5 tube,

before combustion $= 48.2499$	$h = 29.58$	$t = 26.0$
after " $= 48.2529$	$h = 29.76$	$t = 23.5$
Gain in weight $= 0.0030$	$+0.18$	-2.5

Weight of H_2SO_4 tube,

before combustion $= 62.3959$	$h = 29.58$	$t = 26.5$
after " $= 66.1076$	$h = 29.75$	$t = 23.5$
Gain in weight $= 3.7117$	$+0.17$	-3.0

The correction to vacuum for 3.7117 grams of water weighed with brass and platinum weights is 4.1 mg.

Gain in weight of H_2SO_4	$= 3.7117$ grams.
" " P_2O_5	$= 0.0030$
Correction to vacuum	$= 0.0041$
" for t and h, P_2O_5	$= 0.0004$
" " " H_2SO_4	$= 0.0005$
Total H_2O formed	$= 3.7197$
Weight H taken	$= 0.4144$
Weight O combined	$= 3.3053$

$$\text{Atomic weight of oxygen} = \frac{2 \times 3.3053}{0.4144} = 15.953$$

Per cent. H in water $= 11.140$.   Per cent. O in water $= 88.860$.

SERIES III. *Determination 5.*

Weighings of the globe :   Grams.

Exhausted.

Nov.	8th,	7.45 A. M. Tare	$= 0.1127$
	"	11.10 A. M.	$= 0.1125$
	"	12.00 M.	$= 0.1122$
	"	5.00 P. M.	$= 0.1122$
	9th,	8.40 A. M.	$= 0.1121$
	"	9.15 A. M.	$= 0.1119$
	"	12.40 P. M.	$= 0.1120$
	"	4.00 P. M.	$= 0.1121$
	10th,	8.40 A. M.	$= 0.1119$
	"	10.40 A. M.	$= 0.1120$
	11th,	8.40 A. M.	$= 0.1121$
	"	10.15 A. M.	$= 0.1120$

Average Tare $= 0.1120$

Filled with Hydrogen.   Nov. 11th, 12.45 P. M. Tare $= 0.5325$
"   4.00 P. M. $= 0.5348$
"   6.00 P. M. $= 0.5328$
12th, 12.00 M. $= 0.5273$
14th, 8.00 A. M. $= 0.5273$
"   9.30 A. M. $= 0.5273$
"   11.15 A. M. $= 0.5273$

Tare filled with H $= 0.5273$
"   empty $= 0.1120$

Weight H $= 0.4153$

The combustion was started at 11.25 A. M. and stopped at 6 P. M.

Weight of P_2O_5 tube,

before combustion $= 48.1795$ $h = 30.03$ $t = 16.5$
after   " $= 48.1832$ $h = 30.00$ $t = 18.0$

Gain in weight $=$ 0.0037 $- 0.03$ $+ 1.5$

Weight of H_2SO_4 tube,

before combustion $= 64.9625$ $h = 30.03$ $t = 16.5$
after   " $= 67.6832$ $h = 30.00$ $t = 18.0$

Gain in weight $=$ 3.7207 $- 0.03$ $+ 1.5$

Gain in weight of H_2SO_4 $=$ 3.7207 grams.
"   " P_2O_5 $=$ 0.0037
Correction to vacuum $=$ 0.0041

                                      3.7285

Correction for t and h, $H_2SO_4 = - 0.0002$
"   "   " P_2O_5 $= - 0.0002$

Total H_2O formed $=$ 3.7281
Weight H taken $=$ 0.4153

Weight O combined $=$ 3.3128

Atomic weight of oxygen $= \dfrac{2 \times 3.3128}{0.4153} = 15.954$

Per cent. H $= 11.139$.   Per cent. O $= 88.861$.

ATOMIC WEIGHT OF OXYGEN.

Table of Final Results.

SERIES I.

Weight of Hydrogen.	Weight of Water.	Atomic Weight of Oxygen.
0.4233	3.8048	15.977
0.4136	3.7094	15.937
0.4213	3.7834	15.960
0.4163	3.7345	15.941
0.4131	3.7085	15.954

Average $= 15.954 \pm 0.0048$

SERIES II.

0.4112	3.6930	15.962
0.4089	3.6709	15.955
0.4261	3.8253	15.955
0.4197	3.7651	15.942
0.4144	3.7197	15.953

Average $= 15.953 \pm 0.0022$

SERIES III.

0.42205	3.7865	15.943
0.4284	3.8436	15.944
0.4205	3.7776	15.967
0.43205	3.8748	15.937
0.4153	3.7281	15.954
0.4167	3.7435	15.967

Average $= 15.952 \pm 0.0035$

Total average $= 15.953 \pm 0.0017$

Dumas's value $= 15.960 \pm 0.0070$

On examining the table it will be noticed that the mean of the determination by the electrolytic method is the mean of all the determinations combined, and that the probable error of the total average is only about one fourth as great as the error of the nineteen determinations of Dumas, which are incomparably the best that have hitherto been made.

It does not now seem possible to escape from the conclusion that the proportions in which the purest hydrogen that can be made combines with oxygen to form water are those of 2 to 15.953, with a possible error far within the $\frac{1}{100}$ of a single unit.

The question, of course, still remains, Is the hydrogen thus prepared the typical hydrogen element? But this is the same question which must arise in regard to any one of the elementary substances; and all that we can say is, that the evidence in regard to the purity of the hydrogen we have used is as good as any that can be adduced in regard to any one of the elementary substances whose atomic weight has been most accurately determined. The question as regards Prout's hypothesis narrows itself now to this one point; and here we must be content to leave it until further investigation has given us more knowledge in regard to the nature of elementary substances.

The writer at first planned to carry out the investigation on a much larger scale, and for the purpose had blown a globe similar to that represented by Fig. 1, but of five times the capacity, and counterpoised it by the same general method. This globe held twenty-five litres (somewhat over two grams of hydrogen gas), or five times as much as the globe actually used; but the difficulties of carrying out the determinations on this scale led him to reduce the scale of the determinations to that actually adopted; and in view of the results finally reached, it is evident that no appreciable advantage would have been gained from the enormous expenditure of time and labor which the process on a large scale involves. Assuming that the difficulties of preparing pure hydrogen gas on that scale could have been overcome, it would have required from five to seven hours to fill the globe, and four or five days continuously to complete the combustion.

Moreover, after many trials, the writer could not procure a globe that would stand the requisite pressure weighing less than two and one half kilograms, and with this weight and volume it was not possible, with the best balance he could command, to distinguish half a milligram with as much accuracy as he could one tenth of a milligram with the smaller apparatus, while a vastly longer time was required to reach equilibrium. A great deal of time was spent in endeavoring to perfect this larger apparatus, and a very thorough knowledge was acquired of its relative efficiency. The greatest gain that could have been expected in carrying out the

work on this scale would have been the reduction of the probable error to about one half of the present amount, but it is obvious that this gain could be of no importance in the present condition of the science. The accuracy we have reached is far beyond the demands of any analytical work ; and, as we have shown, the theoretical question in regard to Prout's law has been settled so far as analytical work can solve the problem. It now turns solely on the typical character of the material we call hydrogen, when prepared in the purest condition known to modern science.

In considering the bearing of the result now published on Prout's hypothesis, it must be borne in mind that it confirms in a most striking manner the result of Dumas, based on the weight of oxygen which water contains, and in connection with his results furnishes a complete analysis of water, with a degree of accuracy as great as can be expected, or as has ever been obtained, in any analytical work.

Complete Analysis of Water.

Percentage of oxygen after Dumas, ... 88.864 ± 0.0044
Percentage of hydrogen according to the present
     work . . . . 11.140 ± 0.0011
                            100.004 ± 0.0045

It must be remembered that in Dumas's investigation the oxygen alone was weighed, while in the present investigation the hydrogen alone was weighed, and the fact that these two wholly independent analytical results made under such widely different circumstances exactly supplement each other within the limits of probable error, is an evidence of accuracy and a proof of finality which is irresistible.

It would have been highly desirable, if it had been possible, to determine both the oxygen and the hydrogen in one and the same analytical process, as the writer succeeded in doing in the case of silver, bromine, and antimony, and he made many experiments on the reduction of oxide of silver by hydrogen with this view. He succeeded in preparing pure oxide of silver, of definite composition, but the investigation was interrupted by the failure of his sight before he was able to overcome the grave experimental difficulties which the process presented. In view, however, of the present results, it is doubtful whether any advantage would have

been gained by that mode of experimenting, for no more certain confirmation could have been reached than that furnished by a comparison of Dumas's results with those of this paper.

Since this investigation was essentially finished, and the results communicated to the American Academy at their meeting of June 15, 1887, we have received from the author a " Sonderabdruck " from the " Berichte der Deutschen Chemischen Gesellschaft," dated the 26th of July following, and entitled: " E. H. Keiser: Ueber die Verbrennung abgewogener Mengen von Wasserstoff und über das Atomgewicht des Sauerstoffs." In this paper Dr. Keiser distinctly recognises the importance of directly weighing the hydrogen in the determination of the atomic weight of oxygen, and quotes the remarks of Dumas given above. He has also devised a very ingenious method of weighing hydrogen when occluded by palladium ; but the preliminary results he publishes are far from having the degree of accuracy required, and lead us to infer that, like our own preliminary results, they must be vitiated by varying impurities in the hydrogen gas used. The three determinations whose results he publishes gave for the atomic weight of oxygen respectively 15.873, 15.897, and 15.826.

We are sorry if Dr. Keiser has entered on somewhat the same field which we have so long occupied without knowledge of our work. But, as above stated, our investigation was begun more than five years ago ; and the methods employed have been freely explained to the many chemists, both American and European, who have visited Cambridge during the interval. We earnestly hope that Dr. Keiser will carry out his investigation ; for so important a constant as the atomic weight of oxygen cannot be too often verified.

J. P. C. CAMBRIDGE, *December* 15, 1887.

VI.—NOTE ON THE ABSORPTION OF AMMONIA BY ACID SOLUTION IN NITROGEN DETERMINATIONS WITH SODA-LIME.

By I. S. Haynes.

Among the possible sources of error in the determination of nitrogen by the method of Varrentrapp and Will is the failure of the ammonia to be completely absorbed by the acid solution, in case the combustion proceeds very rapidly and the ammonia is considerably diluted with other gases. The following determinations were made to test the effect of rapid combustion on the absorption of ammonia, and, incidentally, the danger of small particles of soda-lime being swept past the asbestos plug into the acid solution. Although undertaken simply as one of the series of exercises in the undergraduate course of study and practice in this laboratory, the results may not be unworthy of record.

The method followed was that described in a previous article of this series[1] as usual in this laboratory, except that the packing of the asbestos plug in the anterior end of the tube and the time of combustion were varied, as shown in the tabular statement herewith. The ammonia was caught in an ordinary Knop and Arendt bulb apparatus (with four bulbs) containing 10 cc. of a rather concentrated standard solution of sulphuric acid, of which 1 cc. corresponded to about 10 mgm. of nitrogen. About 0.25 gram of ammonium sulphate mixed with stearin previously proved to be free from nitrogen, was used for each determination, and furnished ammonia sufficient to neutralise about one half of the acid.

In the determinations numbered 1, 2, and 3 in the table, the anterior asbestos plug was some 2–3 cm. long and packed reasonably tight, as is usually done in our work. In No. 4 it was shorter than usual, and care was taken to pack it very tightly by holding the tube perpendicular with the anterior end down and pressing upward against the asbestos with the flat end of a lead pencil. The soda-lime above furnishes a firm backing, so that the asbestos may be packed as closely as desired. Reversing the tube and tapping it gently, its contents will settle down from the asbestos,

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[1] This Journal 9, 319.

leaving a space which can be closed up as much as necessary by pushing the compacted plug toward the soda-lime. In Nos. 5 to 7 the plug was put in loosely, as might be done by a careless operator. The figures in the table for number of bubbles per minute were estimated by countings of the numbers in different minutes, and are of course only approximate. In Nos. 4 and 7 the effort was made to push the combustion as rapidly as could be done without danger of accident. The flow of gas was much more rapid and the bubbles were much larger than would be the case in any ordinary well conducted analysis. This will readily be seen when we consider that the quantity of diluting gases, from the decomposition of nearly a third of a gram of stearin in each case, was large, and that the time of the combustion was only 12 minutes, instead of from 30 to 60 minutes which the combustion commonly takes. Add that the quantity of acid solution was rather small, only 10 cc., and it is evident that the conditions were very unfavorable for complete absorption of the ammonia. The percentages of nitrogen in Nos. 1 to 4 average 21.14. This figure accords very closely with those obtained by other gentlemen who made determinations of nitrogen in the same material and at the same time by the soda-lime and other methods.

Determinations of Nitrogen in Ammonium Sulphate.

Number.	Asbestos Plug.	Rapidity of Combustion.	Time of Combustion. Minutes.	Number of bubbles per minute. Approximate.	Ammonium Sulphate used. Grams.	Nitrogen found. Per cent.
1	Moderately tight.	Rather slowly.	60	60	0.2457	21.12
2	" "	Moderately fast.	35	70	0.2458	21.15
3	" "	" "	35	70	0.2458	21.15
4	Short and very tight.	Very "	12	90	0.1796	21.16
5	Loose.	Rather "	25	70	0.2630	21.49
6	Short and loose.	Very "	13	85	0.2558	21.69
7	Long "	" "	12	90	0.2928	21.37

Comparison of the figures in the last column of the table shows no loss of nitrogen, even in No. 4, in which the flow of gas was so rapid and the bubbles were so large. To still further test whether ammonia escaped absorption, a second bulb tube with acid solution

was connected with the first so that the gases which came from the first passed through the acid in the second. Even in No. 4, Nessler's test gave no reaction for ammonia in the second tube. It is clear, then, that despite the considerable dilution and extremely rapid flow of the gases through the 10 cc. of acid solution, no ammonia escaped absorption. But it is to be remembered that the quantity of ammonia was only equivalent to about half of the acid in the solution.[1]

The large figures of "nitrogen found" in Nos. 5, 6, and 7 are evidently due to the fine particles of soda-lime which were carried through the loosely packed asbestos plugs by the rapidly passing gases. The necessity of proper packing of the asbestos plug is too obvious to need dwelling upon.

The principal fact brought out in these experiments is that the ammonia, the quantity of which was considerable, was completely absorbed by the acid solution in the cases where the combustion was completed in as short a time as twelve minutes, and where the flow of gas was far more rapid than would occur in any ordinary work. The inference is that the absorption of the ammonia is more certain, and the danger of loss less, than is frequently supposed.

VII.—ON CERTAIN SOURCES OF LOSS IN THE DETERMINATION OF NITROGEN BY SODA-LIME.

By W. O. Atwater and E. M. Ball.

The object of the following experiments was to test the effect of open space between the soda-lime and the upper wall of the tube (channel, as often recommended), and of lengthened time of sojourn of gases in the combustion tube, upon the amount of nitrogen obtained in the form of ammonia in the determination by the soda-lime method. The determinations were conducted by the method described in the previous article of this series[2] as usual in this laboratory, except that:

1st. In some cases the tube was packed so full with soda-lime as to leave no considerable channel, in accordance with our usual practice, while in others less soda-lime was used, enough to fill perhaps from four fifths to two thirds of the whole interior of the tube. The channel left was thus quite large.

[1] See Gassend and Quantin, Ztschr. anal. Chem., 1882, 278.   [2] This Journal **9**, 319.

2d. The anterior layer consisted in some cases of finely powdered soda-lime like that with which the nitrogenous substance is mixed for combustion, instead of the coarse particles with which (to secure more contact between the passing gases and the soda-lime and hence more complete ammonification) we commonly fill the anterior part of the tube.

3d. In some cases the combustion tube and the anterior layer of soda-lime were made longer than usual.

4th. The combustion in some cases occupied the usual time, about three quarters of an hour; in others it was prolonged to two and a half hours, as is done by some chemists.[1]

It seemed desirable that the trials be made with a substance which had been found by other observers frequently to fail to yield all its nitrogen in the form of ammonia. For this casein was selected.[2]

To test the accuracy of the nitrogen determinations when made by soda-lime in the usual way, comparative tests were made with Kjeldahl's method in two specimens. In the determinations with soda-lime, the precautions as to compact filling of tube, heating of anterior layer before applying heat to mixture of soda-lime and nitrogenous material, moderate heating throughout and moderate time of combustion, previously mentioned as usual in this laboratory, were observed. The results of these comparative tests are stated in Table I.

TABLE I.

Nitrogen obtained from Casein by Soda-lime and Kjeldahl Methods.

Casein.	Nitrogen found, per cent.			
	Soda-lime Method.		Kjeldahl Method.	
	Separate Determinations.	Average.	Separate Determinations.	Average.
First specimen.	12.20			
	12.10		12.07	
	12.10			
	12.05	12.11	12.07	12.07
Second specimen.	12.44		12.44	
			12.41	
	12.43	12.44	12.43	12.43

[1] E. g. Nowack, Sitzb. Akad. Wien, **64** Bd., 1871, p. 153; Seegen and Nowack, Pf. Arch. **7**, 1873, 290; Musso, Ztschr. anal. Chem. **16**, 1877, 414.

[2] The analyses were performed by Mr. Ball in the course of practice for students in this laboratory.—W. O. A.

The determinations in the "first specimen" were preliminary, and the duplicates with soda-lime are somewhat wide apart. The "second specimen" was used for the determinations of Table II, in which those of series A are the same as given in Table I.

TABLE II.

Nitrogen Determinations in Casein by Soda-lime under Different Conditions.

| Series. | Length of Tube. | Anterior layer of Soda-lime. | | Packing of Tube. | Time of combustion, approximate. | Color of acid after combustion. | Nitrogen found. |
		Length.	Kind.				
	cm.	cm.					pr ct.
A	38	12	Coarse.	No channel.	45 minutes.	Nearly colorless.	12.44
	38	12	"	"	"	"	12.43
B	38	12	Fine.	Channel.	"	"	12.25
	38	12	"	"	"	Slightly colored.	11.85
	38	12	"	"	"	Very dark.	11.66
C	38	7.5	"	"	"	Amber colored.	12.38
	38	7.5	"	"	"	Colorless.	12.00
	38	7.5	"	"	"	Very dark.	10.51
D	38	12	Coarse.	No channel.	2½ hours.	Slightly colored.	12.27
	38	12	"	"	"	"	12.05
	38	12	"	"	"	"	12.05
	38	12	"	"	"	"	11.96
E	38	12	Fine.	Channel.	"	"	12.44
	38	12	"	"	"	"	12.25
	38	12	"	"	"	"	12.20
	38	12	"	"	"	"	12.15
	38	12	"	"	"	"	11.96
	38	12	"	"	"	"	9.48
F	38	12	"	"	" *	"	3.92
G	43	17	"	"	"	"	3.14
	48	22	"	"	"	"	2.55

* At very high heat.

The percentages of nitrogen, calculated on water-free casein, as before, are stated in detail in Table II, and are concisely recapitulated in Table III.

TABLE III.

Recapitulation of Results of Nitrogen Determinations by Soda-lime under Different Conditions.

Series.	Soda-lime.			Time of combustion.	Nitrogen found.			Average loss of Nitrogen in per cent. of total Nitrogen.
	Anterior layer.		Packing.		Maximum.	Minimum.	Average.	
	Kind.	Length.						
		cm.			per ct.	per ct.	per ct.	per cent.
A	Coarse.	12	No channel.	¾ hour.	12.44	12.43	12.43	...
B	Fine.	12	Channel.	"	12.25	11.66	11.92	3.3
C	"	7½	"	"	12.38	10.51	11.63	6.4
D	Coarse.	12	No channel.	2½ hours.	12.27	11.96	12.08	2.8
E	Fine.	12	Channel.	"	12.44	9.48	11.75	5.5
F	"	12	"	" †	one	det'n.	3.92	68.5
G	"	*	"	"	3.14	2.55	2.85	77.0

*17 and 22 cm.   † At very high heat.

It thus appears that in the experiments of Tables I and II :

When the determinations were made with the precautions named, series A, the duplicate results agreed as closely with each other and with those by the Kjeldahl method as could be desired. This, taken in connection with the facts reported in other papers of this series, constitutes strong evidence of the correctness of the figures for percentages of nitrogen.

In series B a channel was left over the soda-lime in the tube, the other conditions were the same as in A. The percentages of nitrogen fell to an average of 11.92. Taking 12.43, the average of the results obtained in the series A and by the Kjeldahl method, as actual per cent. of nitrogen, this makes a loss of 0.4 per cent. of the weight of the water-free casein, or 3.4 per cent. of the total nitrogen.

Series C was a duplicate of B, except that the anterior layer consisted of fine particles of soda-lime, thus offering slightly less surface for·contact of volatile nitrogenous products with the latter. The percentages of nitrogen were slightly less than in B. The average was 0.8 short of 12.43 per cent., which makes a loss of 6.4 per cent. of the total nitrogen. That the loss in this series averaged so much more than in the previous one may be largely accidental. The loss in the individual determinations ranges from 0.4 to 15.4 per cent. of the total nitrogen. Both the small amounts of nitrogen obtained and the wide variations in the results bear

witness to the error introduced by leaving the channel in the tube.
It seems to us most probable that this loss is mainly due to incom-
plete ammonification of nitrogenous decomposition products. In
series A, in which the tube was closely packed with soda-lime,
these latter were brought more into contact with the heated soda-
lime, i. e. with heated water-vapor, and their nitrogen was com-
pletely changed to ammonia. In series B and C, in which there
was considerable open space in the tube, the contact with soda-
lime would be less intimate, and the ammonification might on that
account be less complete. At the same time it is possible that the
slower current of gas, consequent upon the larger open space,
might, by exposing the ammonia for a longer time to the heat,
lead to dissociation.

In series D the determinations were made by the usual method,
except that the time of combustion was two and a half hours instead
of three quarters of an hour. The loss of nitrogen varied from
1.3 to 3.8 per cent., and averaged 2.8 per cent. of the total nitro-
gen. An article to follow this will give reasons for attributing the
larger part of this loss to dissociation of ammonia during its long
sojourn in the tube, though it may be partly due to incomplete
ammonification. Briefly stated, they are that (1) the longer ex-
posure to heat, which is longer in proportion than the difference in
time would imply, would favor dissociation, and (2) there may
have been lack of moisture from the anterior layer of soda-lime
after the latter had been heated some time, and this lack may have
been unfavorable to complete ammonification but favorable to
dissociation.

In series E the conditions were the same as in D, except that a
channel was left above the soda-lime. The variations in results
and the losses of nitrogen were still greater, the latter ranging from
0.0 to 23.7, average 5.5 per cent. of the total nitrogen. For the
case in which all or nearly all the nitrogen was obtained we have
no satisfactory explanation, and can only state the results as
obtained. That the average loss should be greater and the range
of variation wider with a channel than without it is easily accounted
for, on the ground that the current of outflowing gases would be
slower and the ammonia hence exposed for a longer time to the
heat by which it is dissociated.

The single determination F differed from those of E in that the
heat was as high as the tubes would endure without bursting. The
two in series G differed from those of E in the greater length of

the anterior layer of soda-lime. The nitrogen lost in F and G ranged from 68.5 to 79.5 per cent., or from two thirds to three fourths of the whole. That the lowest results of all should have been obtained with the high heat and very long tubes is easily explained by assuming that the loss of ammonia by dissociation increased with increase of heat and with increase of time of exposure to heat.

To test the working of the soda-lime method with a substance in which the complete ammonification of the nitrogen is more difficult, a series of trials were made with strychnine. The determinations were made by what has been spoken of as our "usual method," except that—

1st. In several cases extra large combustion tubes were employed to allow a larger proportion of soda-lime for mixing with the substance.

2d. In two cases (Nos. 3 and 4 of Table IV) especial pains were taken to put the mixture of fine soda-lime and substance (about 1 part of substance to 40 of soda-lime) along the lower side of the large tube, and to cover it with fine soda-lime, so as to insure passage of the decomposition products through the covering layer of soda-lime, and thus secure more perfect contact of distillation products with soda-lime. The mixture was got into place by aid of a thin narrow tube inserted into the wide combustion tube.

How ineffectual the attempts were to secure complete ammonification of the nitrogen is shown by the figures of Table IV, in which the figures for " Nitrogen found " are those obtained by titration with standard alkali in the usual way. The acid in the bulb tube after combustion was turbid in every case.

Table IV.

Percentages of Nitrogen obtained from Strychnine by Soda-lime.

No.	Substance Used. Gram.	Internal Diameter of Tube. Cm.	Nitrogen Found. Per Cent.
1	.5	1.25	6.47
2	.5	1.25	7.64
3	.2	2.	5.88
4	.2	2.	7.35
5	.1	2.	1.57
6	.1	2.	1.70
7	.1	2.	5.88
8	.1	2.	3.92
9	.05	1.25	1.96

In brief, the greatest care in pulverising the substance finely, mixing intimately with soda-lime, using excessive quantities of soda-lime, and packing the tube closely to avoid channel, were ineffective. Insuring the greatest contact of substance and distillation products with soda-lime and most careful heating evidently do not prevent escape of nitrogen in other forms than ammonia. Attempts to get all the nitrogen as ammonia by Kjeldahl's method were also unsuccessful.

The main outcome of the experiments above detailed may be summarised in few words.

1. In combustions with soda-lime, an open space (channel) in the tube is unnecessary and involves danger of loss of nitrogen. This loss may be due to nitrogenous distillation products which escape ammonification, or to dissociation of ammonia, or to both.

2. Prolonging the time of combustion unduly may induce loss. The most probable cause of this loss would seem to be dissociation of ammonia.

3. High heat increases danger of loss, probably by dissociation of ammonia, especially when open space in the tube or slowness of combustion, or both, leave the gases for a considerable time exposed to the action of the heat and not in intimate contact with the soda-lime.

4. With casein (and the data cited and to be cited in the other articles of this series imply that the same is true for the protein compounds of animal and vegetable tissues generally) sufficient contact between soda-lime and substance at moderately high heat suffices to convert all the nitrogen into ammonia. This is effected by intimate mixture of soda-lime and substance, providing a moderately long anterior layer of soda-lime, close packing of the tube, heating the anterior layer well before the heat is applied to the mixture, and keeping it well heated until the operation is done.

5. There are, however, substances, such as strychnine, which, when heated with soda-lime, yield distillation products that are very difficult of ammonification.

A succeeding article will refer to these points in more detail, discuss loss by incomplete ammonification and dissociation, and refer to a probable explanation which they give of the failure of the soda-lime method to bring satisfactory results in some of the cases most frequently cited in evidence of its unreliability.

THE CHEMICAL STRUCTURE OF THE NATURAL SILICATES.

By F. W. Clarke.

In any attempt to discuss the chemical structure of the inorganic silicates we are met at the outset by difficulties which are partly real and in part imaginary. On the one hand we have to deal entirely with non-volatile solids, of which, because of their fixedness, we cannot certainly ascertain the true molecular weights. They are, furthermore, insoluble and, chemically speaking, non-plastic; that is, they yield but stubbornly to reagents, so that the changes of which they are structurally capable can rarely be studied in the laboratory. These difficulties are very real. On the other hand, most of the definite silicates are natural minerals, and as such are commonly supposed to have a bewildering complexity of constitution. This difficulty is only apparent, not real, and is due to several causes. First, few mineral species occur in a state of even approximate chemical purity; and secondly, many of them, being isomorphous, crystallise together to form seemingly homogeneous bodies to which rational formulae can hardly be assigned. Impurities, indefinite crystalline mixtures, and defective analyses account for many apparent complications. Eliminate from any group of natural silicates these disturbing conditions, and we shall find in every case a simplicity of composition far removed from the complexity which is popularly assumed. Even on theoretical grounds we should expect simplicity of structure. The mineral silicates are, as a rule, exceedingly stable compounds, while complex molecules are relatively unstable. They are formed in nature under conditions of high temperature, or are deposited from solutions in which many reactions are simultaneously possible; circumstances that are strongly adverse to any great complications of structure. Finally, they are quite limited in number, only a few hundred at most being known; whereas, if complexity was the rule among them, slight variations in origin would produce great variations in character and millions of different minerals would be generated. That few substitutions occur is presumptive evidence that only few are possible, and hence simplicity of con-

stitution is to be inferred. In fact we find the same small range of mineral species occurring under the same associations in thousands of widely separated localities, a few typical forms containing a few of the commonest metals being almost universally distributed. The longer the evidence is considered, the more overwhelming the argument for simple silicate structures becomes.

Suppose now that for any given silicate the empirical composition has been ascertained, how can its chemical structure be determined? We cannot measure its vapor density and so deduce its molecular weight; but the problem is not therefore necessarily hopeless. Several lines of available evidence are open. In some cases the compound may be synthetically reproduced in the laboratory, a kind of mineralogical investigation in which rapid progress is now being made. Again, the constant association of the species with certain others sheds light upon its genesis, and still oftener its alterations in nature furnish important details. An alteration product, despised by the crystallographer, is really a record of chemical change, and such products may be of the highest scientific interest. In a few researches they have been produced artificially by reactions which were prolonged for months at a time, and so a mass of evidence is slowly accumulating, strictly analogous in kind to that which the organic chemist chiefly depends upon for ascertaining the structure of a hydrocarbon. All these lines of evidence are legitimate, and all converge towards truly scientific conclusions. We know that certain silicates originated together, and that each alters in certain definite ways; and from these facts we may draw perfectly fair inferences as to chemical structure, and deduce rational formulae which shall give fuller expression to our knowledge. The evidence for such formulae is less perfect than that at the command of the carbon chemist, but it is none the less substantial so far as it goes. It is, furthermore, cumulative.

About three years ago, while I was working tentatively at the problem now under discussion, I received for examination certain specimens of topaz which were deeply altered upon their surfaces. Upon investigation the alteration product proved to be a variety of muscovite, and a study of the empirical formulae of the two minerals revealed an unexpected relation between them. Further study brought out more extended relations connecting them with several other silicates, and by a natural series of steps I was led to adopt as a working hypothesis the supposition that double salts

might be regarded as substitution derivatives of normal salts. This hypothesis, since then steadily applied to the discussion of the silicates, appears to be supported by a weighty mass of evidence, and it leads to the development of a series of structural formulae which satisfy many conditions. They express and interpret known relations, lead to the detection of others, and point out suggestive and profitable lines of research. By these tests any hypothesis must stand or fall, and one which, meeting them successfully, has at the same time philosophical significance, may be fairly looked upon as valid.

That the great majority of the natural silicates are double salts need hardly be stated, and that a very great number of them contain aluminum is also a commonplace of chemistry. Of the latter some are orthosilicates, and some are meta-compounds ; and the problem is to show how each series may be derived from its corresponding normal salt. As the orthosilicates are the most important, we may begin with their consideration. They represent the maximum of complication and offer the greatest difficulties.

Fortunately, the orthosilicate of aluminum, $Al_4(SiO_4)_3$, occurs in nature as the mineral xenolite. This species, which is now well established, was long thought to be an impure variety of fibrolite, Al_2SiO_5 ; and in their optical properties the two are apparently identical. Fibrolite bears the closest of relations to its isomer, andalusite ; and to the latter, topaz, $Al_2SiO_4F_2$, is crystallographically akin. Topaz, as I have already stated, alters into muscovite, $Al_3KH_2(SiO_4)_3$; and so also does eucryptite, $AlLiSiO_4$. To these compounds we may add paragonite, which is merely a sodium mica, and we have at least six silicates, including the normal salt, which are all evidently related to each other. That their empirical formulae show little or no connection is due to the fact that they do not represent true molecular weights, and on this point our fundamental hypothesis gives us a key to the problem. If we triple the formulae given for fibrolite, topaz, and eucryptite, the substitution theory which I have suggested at once becomes applicable, and the derivation of all the others from xenolite is easy. The following structures will make this conception clear :

$$Al \diagdown \begin{matrix} SiO_4 \equiv Al \\ SiO_4 \equiv Al \\ SiO_4 \equiv Al \end{matrix} \qquad Al \diagdown \begin{matrix} SiO_4 \equiv (AlO)_3 \\ SiO_4 \equiv Al \\ SiO_4 \equiv Al \end{matrix} \qquad Al \diagdown \begin{matrix} SiO_4 \equiv (AlF_2)_3 \\ SiO_4 \equiv Al \\ SiO_4 \equiv Al \end{matrix}$$

Xenolite.   Fibrolite.   Topaz.

$$Al \diagdown \begin{array}{l} SiO_4 \equiv KH_2 \\ SiO_4 \equiv Al \\ SiO_4 \equiv Al \end{array}$$
<div align="center">Muscovite.</div>

$$Al \diagdown \begin{array}{l} SiO_4 \equiv NaH_2 \\ SiO_4 \equiv Al \\ SiO_4 \equiv Al \end{array}$$
<div align="center">Paragonite.</div>

$$Al \diagdown \begin{array}{l} SiO_4 \equiv Li_3 \\ SiO_4 \equiv Al \\ SiO_4 \equiv Al \end{array}$$
<div align="center">Eucryptite.</div>
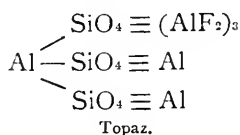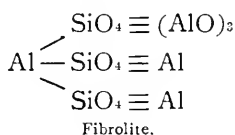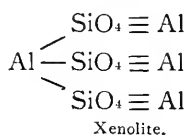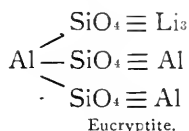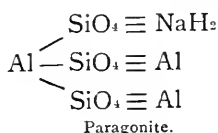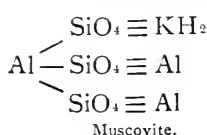
In the second of these formulae the univalent group $-Al = O$ is assumed, and in the third we have the corresponding group $-Al = F_2$. I think no chemist will regard these assumptions as strained.

Now the foregoing symbols all represent a series of salts derived from the first one by various substitutions of a single aluminum atom. But further replacements are theoretically possible, and the following minerals seem to illustrate them:

$$Al \diagdown \begin{array}{l} SiO_4 \equiv (AlO)_3 \\ SiO_4 \equiv (AlO)_3 \\ SiO_4 \equiv Al \end{array}$$
<div align="center">Dumortierite.</div>

$$Al \diagdown \begin{array}{l} SiO_4 \equiv \\ SiO_4 \equiv \\ SiO_4 \equiv Al \end{array} \Bigr\} Ca_3$$
<div align="center">Grossularite.</div>

$$Al \diagdown \begin{array}{l} SiO_4 \equiv CaH \\ SiO_4 \equiv CaH \\ SiO_4 \equiv Al \end{array}$$
<div align="center">Prehnite.</div>

$$Al \diagdown \begin{array}{l} SiO_4 \equiv NaH_2 \\ SiO_4 \equiv NaH_2 \\ SiO_4 \equiv Al \end{array}$$
<div align="center">Natrolite.</div>
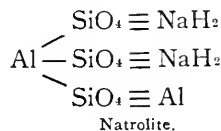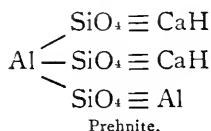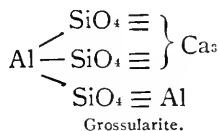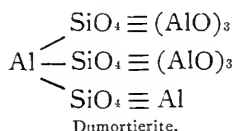
Dumortierite, which has been little studied, appears to be related to fibrolite, and the formulae exhibit a relation. Grossularite, the lime alumina garnet, is a common associate of muscovite, a fact which lends verisimilitude to the formula given above. The other two formulae represent the known composition of prehnite and natrolite, but whether they indicate any deeper relations is not yet proven. They do, however, suggest lines of investigation, and so far fulfill a useful purpose. If they are true, prehnite should be derivable from garnet, and garnet and muscovite ought to be mutually derivable from each other. That garnets do alter into micas is already well known, although the exact character of the change is undetermined, and the micas involved in the reaction appear to be more complex than muscovite.

Returning now to fibrolite, we find that it is a mineral which is liable to alter through a process of hydration. Some of its alteration products have been described as species, notably under the names wörthite and westanite, the latter being apparently the final

product. Certain other species of the same group frequently undergo a sort of degradation into clays, which, unfortunately, are often too impure to admit of precise formulation. Still, of the several clays which are certainly definite, two seem to fall into series with fibrolite and westanite, as the following structures show :

$$
\begin{array}{c}
\nearrow SiO_4 \equiv (AlO)_3 \\
Al \overline{} SiO_4 \equiv Al \\
\searrow SiO_4 \equiv Al \\
\text{Fibrolite.}
\end{array}
\qquad
\begin{array}{c}
\nearrow OH \\
Al \overline{} SiO_4 \equiv Al \\
\searrow SiO_4 \equiv Al \\
\text{Westanite.}
\end{array}
$$

$$
\begin{array}{c}
\nearrow OH \\
Al \overline{} SiO_4 \equiv H_3 \\
\searrow SiO_4 \equiv Al \\
\text{Kaolinite.}
\end{array}
\qquad
\begin{array}{c}
\nearrow OH \\
Al \overline{} SiO_4 \equiv H_3 \\
\searrow SiO_4 \equiv H_3 . \\
\text{Montmorillonite.}
\end{array}
$$
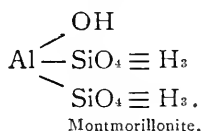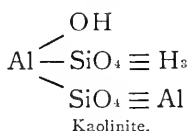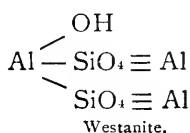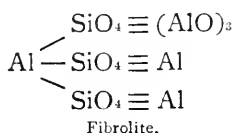
Now, suggestive as these formulae are, they represent only a selection out of a much larger number, all of which seem to follow essentially the same structural rule. If the case rested here it would still be a strong one, but it becomes even stronger when we study some of the more complex orthosilicates, and some of the silicates containing other inorganic acids. In most of the foregoing instances we have one aluminum atom linked with three of the orthosilicic groups, and making a sort of fundamental nucleus to which the other atoms of each molecule are attached. But in many cases we seem to have a semi-polymerisation of that nucleus which results in the elimination of one of the silicas, leaving a new group of atoms which may be represented as follows :

$$
\begin{array}{c}
\nearrow SiO_4 \equiv \\
Al \overline{} SiO_4 \equiv \\
\searrow SiO_4 = \\
\nearrow SiO_4 \equiv \\
Al \overline{} SiO_4 \equiv \\
\searrow SiO_4 \equiv
\end{array}
$$
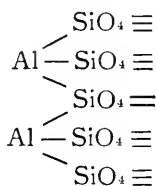
This group, saturated by various bases, seems to exist in many natural silicates, notably among the iron and magnesian micas ; and from it certain mixed salts, like sodalite and nosean, may be represented as derived. Thus, to cite a few examples, we may write :

$$
\begin{array}{l}
\diagup \text{SiO}_4 \equiv \text{FeH} \\
\text{Al} - \text{SiO}_4 \equiv \text{FeH} \\
\diagdown \text{SiO}_4 = \text{K}_2 \\
\diagup \\
\text{Al} - \text{SiO}_4 \equiv \text{FeH} \\
\diagdown \text{SiO}_4 \equiv \text{FeH}
\end{array}
$$
Annite.

$$
\begin{array}{l}
\diagup \text{SiO}_4 \equiv \text{Na}_3 \\
\text{Al} - \text{SiO}_4 \equiv \text{Al} \\
\diagdown \text{SiO}_4 = \text{Na}_2 \\
\diagup \\
\text{Al} - \text{SiO}_4 \equiv \text{Al} \\
\diagdown \text{Cl}
\end{array}
$$
Sodalite.

$$
\begin{array}{l}
\diagup \text{SiO}_4 \equiv \text{Na}_3 \\
\text{Al} - \text{SiO}_4 \equiv \text{Al} \\
\diagdown \text{SiO}_4 = \text{Na}_2 \\
\diagup \\
\text{Al} - \text{SiO}_4 \equiv \text{Al} \\
\diagdown \text{SO}_4 - \text{Na}
\end{array}
$$
Nosean.

$$
\begin{array}{l}
\diagup \text{SiO}_4 \equiv \text{Na}_3 \\
\text{Al} - \text{SiO}_4 \equiv \text{Al} \\
\diagdown \text{SiO}_4 = \text{Na}_2 \\
\diagup \\
\text{Al} - \text{SiO}_4 \equiv \text{Al} \\
\diagdown \text{S} - \text{Na.}
\end{array}
$$
Ultramarine.
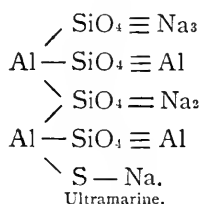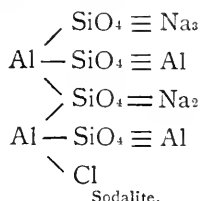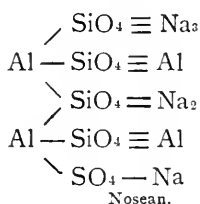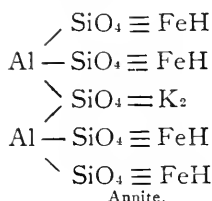
The last of these four formulae is purely hypothetical and rests upon the recognised mineralogical analogies between lapis lazuli and nosean. It is, however, a formula which should be capable of synthetic verification, for ultramarine, itself a product of synthesis, yields many derivatives, the formation of which can be systematically studied. Possibly the lines of research followed by Lemberg, in his work on the alterations of elacolite, may be fitly applied to the investigation of lapis lazuli. As for annite, I have discussed its relations, together with those of the lithia micas, in a previous paper,[1] in which I have also given some suggestions concerning the part played by fluorine in lepidolite, cryophyllite, and phlogopite. Sodalite and nosean were considered in a still earlier paper,[2] in connection with cancrinite, nephelite, and other species. It is hardly necessary to repeat either discussion here.

Passing now to the metasilicates, we find ourselves, as regards the aluminous salts, at some disadvantage. The normal compound, $\text{Al}_2(\text{SiO}_3)_3$, is not known to exist by itself in nature, although certain of its derivatives are common. Its formula, however, may be written in two ways, as follows, and to one of these types some of the double aluminous metasilicates should conform :

I.
$$
\begin{array}{l}
\quad\quad \diagup\!\!\diagup \text{SiO}_3 \\
\text{Al} \\
\quad \diagdown \text{SiO}_3 \\
\text{Al} \diagup \\
\quad \diagdown\!\!\diagdown \text{SiO}_3
\end{array}
$$

II.
$$
\begin{array}{l}
\quad\quad \diagup \text{SiO}_3 \diagdown \\
\text{Al} - \text{SiO}_3 - \text{Al.} \\
\quad\quad \diagdown \text{SiO}_3 \diagup
\end{array}
$$
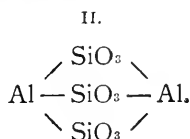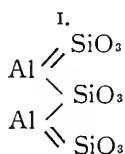
[1] Amer. Journ. Sci., Nov. 1886.　　[2] Amer. Journ. Sci., April, 1886.

Which of the two is best sustained by evidence?

To answer this question we may appeal to several well known minerals, such as spodumene, $AlLi(SiO_3)_2$, jadeite, $AlNa(SiO_3)_2$, leucite, $AlK(SiO_3)_2$, and pyrophyllite, $AlH(SiO_3)_2$. All of these can be generalised under one formula, thus:

$$Al \underset{\diagdown SiO_3 - R,}{\overset{\diagup SiO_3}{\Big\langle}}$$
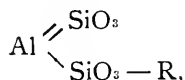
which is directly derivable from normal salt No. 1, and is not derivable from No. 2. Furthermore, kyanite, an isomer of fibrolite, Al_2SiO_5, is regarded by Groth and others as a basic metasilicate, for reasons which need not be reconsidered here. As such its formula is $Al_2(SiO_3)O_2$, which may be derived from either of the formulae for the normal compound. But pyrophyllite often occurs as the gangue of kyanite, which suggests a genetic relation between the two, and so makes it highly probable that the latter mineral should be written

$$\begin{array}{c} Al \overset{\diagup SiO_3}{\underset{\diagdown O}{\Big\langle}} \\ Al \overset{\diagup}{\underset{\diagdown O}{\Big\langle}} \end{array}$$
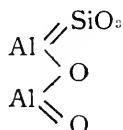
rather than as a derivative of the second formula for $Al_2(SiO_3)_3$. Formula No. 1, then, is the more probable formula for aluminum metasilicate. Two isomers may be possible, but the evidence so far favors only one compound.

In addition to orthosilicic and metasilicic acids, at least two other silicic acids correspond to known salts. These are the compounds $H_2Si_2O_5$ and $H_4Si_3O_8$. Still more are possible, but it is not necessary to assume them in order to account for known minerals. Derived from $H_2Si_2O_5$ we have a few species, notably petalite, $AlLi(Si_2O_5)_2$, which is the equivalent of spodumene in structure. The other acid, $H_4Si_3O_8$, is represented only by the species albite and orthoclase, $AlNaSi_3O_8$ and $AlKSi_3O_8$ respectively. If we triple these formulae we have structures quite analogous to the orthosilicates, in which the normal aluminum salt $Al_4(Si_3O_8)_3$ is the starting point for derivation. Now it is universally believed, in accordance with the views of Sterry Hunt and Tschermak, that the triclinic feldspars consist of various mixtures between albite and anorthite as two extremes. If our fundamental hypothesis is true, each of these minerals is derived

by substitution from a normal salt, and the formulae so deduced become strikingly suggestive :

$$\begin{array}{l} \diagup SiO_4 \equiv \\ Al - SiO_4 \equiv Al \\ \diagdown SiO_4 \equiv Al \end{array} \qquad \begin{array}{l} \diagup Si_3O_8 \equiv \\ Al - Si_3O_8 \equiv Al \\ \diagdown Si_3O_8 \equiv Al \end{array}$$
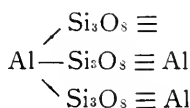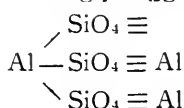
Anorthite is the lime salt corresponding to the first formula, and albite is the soda salt corresponding to the second. Another comparison is even more striking. The four silicates most frequently associated with each other in granite veins are muscovite, garnet, albite or orthoclase, and tourmaline. Tourmaline, according to the analyses made by Mr. Riggs in the laboratory of the United States Geological Survey, is always represented by the general formula $R'_9BO_2(SiO_4)_2$, in which at least the equivalent of R'_3 is present as aluminum. This gives us the following quartette of formulae :

$$\begin{array}{l} \diagup SiO_4 \equiv KH_2 \\ Al - SiO_4 \equiv Al \\ \diagdown SiO_4 \equiv Al \\ \quad \text{Muscovite.} \end{array} \qquad \begin{array}{l} \diagup SiO_4 \equiv \\ Al - SiO_4 \equiv \Big\} Ca_3 \\ \diagdown SiO_4 \equiv Al \\ \quad \text{Garnet.} \end{array}$$

$$\begin{array}{l} \diagup BO_2 \\ Al - SiO_4 \equiv R_3 \\ \diagdown SiO_4 \equiv R_3 \\ \quad \text{Tourmaline.} \end{array} \qquad \begin{array}{l} \diagup Si_3O_8 \equiv K_3 \\ Al - Si_3O_8 \equiv Al \\ \diagdown Si_3O_8 \equiv Al \\ \quad \text{Orthoclase.} \end{array}$$
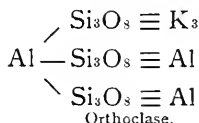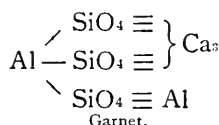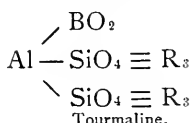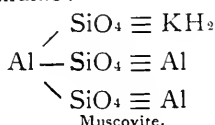
The suggestiveness of these symbols can hardly be questioned. All four are covered by the one general hypothesis ; and tourmaline, furthermore, is known to alter into muscovite.

Leaving the aluminous salts, the other silicates present few structural difficulties. Isomorphous mixtures become perhaps more common, but when they are resolved into their constituents relatively simple compounds are found. The commoner bivalent metals form both ortho- and metasilicates, and to them the substitution hypothesis, as a rule, easily applies. Only in the metasilicate series do we find notable difficulties, and they may be avoided by the assumption of polymeric molecules. Thus, instead of $R''SiO_3$ we should write $R''_2(SiO_3)_2$, in which one atom of R'' becomes replaceable. This conception is by no means new, and is indeed quite commonly in use ; but I may be permitted to cite one item of evidence in its favor. When solutions of calcium chloride and sodium metasilicate are mixed, a white precipitate

of calcium metasilicate is thrown down. This reaction I have studied under various conditions of temperature and concentration, and I find that when the precipitated salt is carefully dried over sulphuric acid it has the composition $2CaSiO_3 . 5H_2O$. That is, the double molecule $Ca_2Si_2O_6$ is required in order to avoid a formula containing a half molecule of water. By itself this fact is not of weighty importance, but it counts for something in confirmation of the prevalent views.

Concerning mixed silicate molecules, partly ortho- and partly meta-compounds, I have nothing at present to say. Such silicates undoubtedly exist, as well as aluminous silicates derived from normal salts of magnesia or lime. Nor do I venture to assert that all known silicates are as yet interpretable by simple structural means. There are many outstanding cases which still seem very obscure, but which I confidently expect will be cleared up in time. The micas, chlorites, and scapolites especially need a great deal of farther study. Various theories have been proposed to account for the composition of these groups, but not one is absolutely conclusive and satisfactory. The new method of discussion which I have proposed is yet to be fully applied to these minerals, but a wider knowledge of their variations is essential to its complete application. Whether the method shall be finally established as valid remains to be seen, but its results so far at least entitle it to respectful consideration. As a working hypothesis the substitution theory has value, even though it should be ultimately overthrown.

In conclusion, there is one question to be considered. With the silicates the supposition that double salts are substitution derivatives of normal salts appears to work exceedingly well. But how about double salts in general? With such compounds as the sulphates, chromates, tartrates, oxalates, etc., there seem to be few difficulties; but with the double haloids, acetates, formates, etc., the case is not so clear. Their explanation is troublesome, at least in accordance with current views concerning the valency of their acid radicles; but those views are not absolutely incapable of modification. There may be exceptions to the general hypothesis of derivation, but chemists are not likely to be satisfied with partial theories, and all double salts ought to come under one common law. Toward that ultimate purpose the present paper tends, even though the road which it opens may not reach the final goal.

XXXIV.—ON THE AMINE SALTS OF BENZENE-SULPHONIC ACID.[1]

By T. H. Norton and J. H. Westenhoff.

Hitherto no amine derivatives have been prepared from the numerous aromatic sulphonic acids, with the exception of the aniline salt of benzene-sulphonic acid obtained by Gericke,[2] but not analysed.

It seemed desirable to fill to some extent this void in the list of sulphonates, and for that purpose a number of salts were prepared by the combination of various fatty and aromatic amines with benzene-sulphonic acid, the simplest member of its group.

The sulphonic acid used in the following experiments was prepared by the method of Michael and Adair,[3] which consists in simply heating together equal parts of benzene and concentrated sulphuric acid with a condenser for about 30 hours. About three quarters of the benzene was changed into acid by this operation. The product was poured into water and neutralised in the ordinary manner by the addition of barium carbonate. By the careful addition of the necessary amount of sulphuric acid to the solution of barium sulphonate, the base was entirely removed, and the filtered solution contained the pure sulphonic acid. This solution of benzene-sulphonic acid, or the crystals obtained from it by concentration, were used in the preparation of the salts to be described.

Benzene-sulphonic acid.—According to Otto[4] this acid is obtained in the form of very deliquescent needles, which, when dried over sulphuric acid, contain $1\frac{1}{2}$ molecules of water of crystallisation. Hübner[5] states that it consists of large plates with 1 molecule of water of crystallisation, and gives the melting point as 40°–42°.

By careful concentration of the aqueous solution of the acid we obtained it in the form of fine needles, exceedingly deliquescent. No traces of crystallisation in plates could be observed. The needles when thoroughly dried between bibulous paper melted at 43°–44°. On heating the fused acid to 150°, thereby driving off

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[1] The material of this and the two following papers was prepared in connection with an extended study of the derivatives of typical aromatic sulphonic acids, now being prosecuted in this laboratory.—T. H. N.

[2] Ann. Chem. (Liebig) **100**, 217.

[3] Ber. d. chem. Ges. **10**, 585.

[4] Ann. Chem. (Liebig) **141**, 369.

[5] Ann. Chem. (Liebig) **223**, 240.

the water of crystallisation, the melting point of the anhydrous acid was found to be 50°–51°. The anhydrous acid solidifies in a fibrous crystalline mass. It decomposes slowly above 155°. The hydrated crystals are insoluble in ether and carbon disulphide, very slightly soluble in benzene, and exceedingly soluble in alcohol and water.

Methylamine benzene-sulphonate, $C_6H_5.SO_3H.NH_2CH_3$.—This salt was obtained by adding a 33 per cent. aqueous solution of methylamine in slight excess to the concentrated solution of benzene-sulphonic acid. On concentration by boiling the excess of the amine was driven off and crystals of the salt were formed. The salt crystallises in fine white needles, joined together in rosettes, and is not easily obtained otherwise than in a fibrous mass, on account of its extreme solubility. The crystals contain no water of crystallisation and are very deliquescent. They melt at 147°. The salt is insoluble in benzene, ether, and carbon disulphide. It is soluble in its own weight of alcohol and of cold water, and in a much smaller quantity of hot water.

Not only this methylamine salt, but also all of the amine derivatives of benzene-sulphonic acid crystallise in the anhydrous state, a property which they share in common with most ammonium salts of the sulphonic acids. The crystalline salts of the metallic bases with these acids contain, on the contrary, almost invariably one or more molecules of water of crystallisation.

This salt, dried in a vacuum over sulphuric acid, lost no water on heating to 110°.

0.2718 gram of the salt thus dried gave 0.3402 gram of barium sulphate, equal to 0.0467 gram of sulphur, or 17.17 per cent.

	Calculated for $C_7H_{11}NO_3S$.	Found.
S	16.93	17.17

Analysis of Sulphonates.—The method used for the sulphur determination in this instance, as well as in the analyses of the salts to be described later, was that indicated some years since by Pearson.[1] This method of oxidising organic substances containing sulphur, which never received the attention it merited, is admirably adapted for the analysis of sulphonates, and certainly surpasses in simplicity and economy the processes now in vogue in our laboratories.

[1] Ztschr. anal. Chem. **9,** 271.

As no mention is made of it in the majority of our works on analytical chemistry, we give a brief description of the details of the operation.

The substance to be analysed is mixed in a porcelain dish with potassium chlorate. This mixture is covered by a funnel, the neck of which is bent at a right angle in order to prevent loss by spattering. Nitric acid (1.36 sp. gr.) is gradually added, and the dish gently warmed until complete solution is effected. The excess of acid is driven off by evaporation to dryness, and the sulphuric acid is precipitated from the solution of the residual potassium salts in the ordinary manner.

This method gives almost invariably good results with sulphonates. The only difficulty experienced is an occasional tendency to spatter, and this is obviated by careful attention during the operation. This tendency is more marked in the case of salts with the aromatic amines, and especially in the case of the aniline salt, which on several occasions entered into violent combustion on the addition of the nitric acid.

Dimethylamine benzene-sulphonate, $C_6H_5SO_3H.NH(CH_3)_2$.— The preparation is similar to that of the monamine salt. It crystallises in thin white plates which melt at 110°. This salt is anhydrous, but very deliquescent. It is insoluble in ether, benzene, and carbon disulphide. It is soluble in two and one-half parts of alcohol, in two parts of cold water, and in a very small amount of hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

I. 0.4384 gram of the salt thus dried gave by Pearson's method 0.5065 gram of $BaSO_4$, equal to 0.0695 gram of S or 15.84 per cent.

II. 0.2766 gram gave 0.3175 gram of $BaSO_4$, equal to 0.0436 gram of S or 15.72 per cent.

	Calculated for $C_8H_{13}NO_3S$.	I.	II.
S	15.76	15.84	15.72

Trimethylamine benzene-sulphonate, $C_6H_5SO_3H.N(CH_3)_3$.—The preparation was the same as that of the preceding salts. It is obtained in the form of a mass of white fibrous crystals which are somewhat deliquescent and melt at 88°–89°. The salt is anhydrous. It is insoluble in ether, benzene, and carbon disulphide. It is

soluble in its own weight of alcohol and of cold water, and is very soluble in hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

0.1687 gram of the salt thus dried gave by Pearson's method 0.1762 gram of $BaSO_4$, equal to 0.0242 gram of S or 14.35 per cent.

	Calculated for $C_9H_{15}NO_3S$.	Found.
S	14.75	14.35

Ethylamine benzene-sulphonate, $C_6H_5SO_3H.NH_2C_2H_5$.— The preparation is similar to that of the methyl salts.   It is obtained in the form of a fibrous mass of white crystals which are anhydrous and melt at 92°.   The salt is insoluble in ether, benzene, and carbon disulphide.   It is soluble in its own weight of alcohol or cold water, and very soluble in hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

I. 0.5239 gram of the salt thus dried gave 0.5977 gram of $BaSO_4$, equal to 0.082 gram of S or 15.51 per cent.

II. 1.0646 grams gave 1.2283 grams $BaSO_4$, equal to 0.1687 gram S or 15.85 per cent.

III. 0.9497 gram gave by Will and Varrentrapp's method 0.0632 gram of N, equal to 6.65 per cent.

	Calculated for $C_8H_{13}NO_3S$.	Found. I.	II.
N	6.89	6.65	...
S	15.76	15.85	15.51

Diethylamine benzene-sulphonate, $C_6H_5SO_3H.NH(C_2H_5)_2$.— This salt is prepared by adding the pure amine to the concentrated solution of the acid.   On concentration it crystallises in long, color- less, anhydrous prisms which are not very deliquescent.   The melting point is 139°.   It is insoluble in ether, benzene, and carbon disulphide.   It is soluble in $4\frac{1}{2}$ parts of alcohol, $1\frac{1}{2}$ parts of cold water, and less than 1 part of hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

I. 0.6791 gram of the salt thus dried gave 0.6758 gram of $BaSO_4$, equal to 0.0928 gram of S or 13.66 per cent.

II. 0.4904 gram of the salt gave 0.4912 gram of $BaSO_4$, equal to 0.0674 gram of S or 13.75 per cent.

	Calculated for $C_{10}H_{17}NO_3S.$	Found. I.	II.
S	13.85	13.66	13.75

Triethylamine benzene-sulphonate, $C_6H_5SO_3H.N(C_2H_5)_3$. — Preparation similar to that of the preceding salt. It crystallises in the form of rhombic plates which are anhydrous, but very deliquescent. Melting point 120°–121°. It is insoluble in ether, benzene, and carbon disulphide. It is soluble in 1½ parts of alcohol or cold water, and is very soluble in hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

0.5248 gram of the salt thus dried gave 0.4785 gram of $BaSO_4$, equal to 0.657 gram of S or 12.51 per cent.

	Calculated for $C_{12}H_{19}NO_3S.$	Found.
S	12.45	12.51

Isobutylamine benzene-sulphonate, $C_6H_5SO_3H.NH_2.CH_2.CH$ $(CH_3)_2$.—Preparation similar to that of the preceding salts. The salt crystallises in slender white prisms which are anhydrous and but slightly deliquescent. It melts at 132°. It is insoluble in ether, benzene, and carbon disulphide. It is soluble in 1 part of alcohol, 2 parts of cold water, and 1 part of hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

I. 0.3964 gram of the salt thus dried gave 0.4102 gram of $BaSO_4$, equal to 0.0563 gram of S or 14.2 per cent.

II. 0.459 gram of the salt gave 0.4745 gram of $BaSO_4$, equal to 0.0651 gram of S or 14.2 per cent.

	Calculated for $C_{10}H_{17}NO_3S.$	Found. I.	II.
S	13.86	14.2	14.2

Isoamylamine benzene-sulphonate, $C_6H_5.SO_3H.NH_2C_5H_{11}$.— Preparation similar to that of the methyl salts. The salt crystallises in thin white plates which are anhydrous, but very deliquescent. It melts at 107°. It is insoluble in ether, benzene, and carbon disulphide. It is soluble in its own weight of cold water or alcohol, and very soluble in hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

0.3079 gram of the salt thus dried gave 0.2867 gram of $BaSO_4$, equal to 0.0393 gram of S or 12.78 per cent.

	Calculated for $C_{11}H_{19}NO_3S$.	Found.
S	13.06	12.78

Aniline benzene-sulphonate, $C_6H_5SO_3H \cdot NH_2C_6H_5$.—This salt was prepared by adding a very concentrated solution of the acid to aniline. A precipitate was formed which, however, readily dissolved on warming. This solution on cooling deposits the crystals in the form of very fine silky white needles, anhydrous and not deliquescent. The salt melts at 235°–237°, undergoing slight decomposition at the same time. It is insoluble in benzene, carbon disulphide, and cold ether, but dissolves slightly in hot ether. It is soluble in 8 parts of alcohol or cold water, and in 5 parts of hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

I. 0.1703 gram of the salt thus dried gave 0.15 gram of $BaSO_4$, equal to 0.0206 gram of S or 12.09 per cent.

II. 0.17 gram of the salt gave 0.15 gram of $BaSO_4$, equal to 0.0206 gram of S or 12.11 per cent.

III. 0.1765 gram of the salt gave 0.1577 gram of $BaSO_4$, equal to 0.0216 gram of S or 12.12 per cent.

	Calculated for $C_{12}H_{13}NO_3S$.	I.	Found. II.	III.
S	12.74	12.09	12.11	12.12

As already mentioned, the determination of the sulphur in this aniline salt was less simple than in the other cases. The addition of nitric acid to the mixture of the salt and potassium chlorate always occasioned a violent reaction, accompanied by spattering and even combustion, during which probably a slight loss occurred, thus accounting for the low results in all the analyses.

This salt was prepared by Gericke[1] by dropping aniline in a warm solution of benzene sulphonic acid. He obtained long, lustrous, silky needles which crystallised in radial groups and which had a reddish color. The salt was easily soluble in water and alcohol, scarcely soluble in ether. He found the melting point to be 201°, but made no analysis.

[1] Ann. Chem. (Liebig) **100**, 217.

The statement with regard to the color and melting point would indicate the presence of impurities in Gericke's product.

Diphenylamine benzene-sulphonate, $C_6H_5SO_3H . NH(C_6H_5)_2$.—This salt was prepared by adding the concentrated solution of the acid to an alcoholic solution of diphenylamine. The crystals separate out on driving off the alcohol. The salt crystallises in fibrous masses of needles which are anhydrous and of a light bluish gray color. It melts at 115°–117°. It is insoluble in ether and carbon disulphide. It is soluble in 65 parts of benzene and in four parts of alcohol. It is decomposed by water.

The salt dried in vacuo over sulphuric acid lost no weight on heating to 110°.

0.479 gram of the salt thus dried gave 0.3272 gram of $BaSO_4$, equal to 0.0449 gram of S or 9.59 per cent.

	Calculated for $C_{18}H_{17}NO_3S$.	Found.
S	9.60	9.59

Orthotoluidine benzene-sulphonate, $C_6H_5SO_3H . NH_2C_7H_7$.—This salt was likewise obtained by adding the aqueous solution of the acid to an alcoholic solution of o-toluidine. The precipitate obtained on driving off the alcohol was dissolved in hot benzene, and the salt crystallised readily on allowing the solution to cool. The crystals form a mass of wool-like filaments, are anhydrous, and possess a slight reddish tinge. The salt melts at 137°. It is insoluble in carbon disulphide and cold benzene. It is soluble in 30 parts of cold water, 2 parts of hot water, 1½ parts of alcohol, 40 parts of hot benzene, and very slightly soluble in ether.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

I. 0.5014 gram of the salt thus dried gave 0.4509 gram of $BaSO_4$, equal to 0.0621 gram of S or 12.34 per cent.

II. 0.5455 gram of the salt gave 0.4969 gram of $BaSO_4$, equal to 0.0682 gram of S or 12.39 per cent.

	Calculated for $C_{13}H_{15}NO_3S$.	Found. I.	II.
S	12.08	12.34	12.39

a-Naphthylamine benzene-sulphonate, $C_6H_5SO_3H.NH_2C_{10}H_7$.—Preparation similar to that of the preceding salt. It crystallises in very fine needles which assume a radial structure, are anhydrous,

and possess a slight grayish tint. It melts at 225° with slight decomposition. It is insoluble in ether, benzene, carbon disulphide, and cold water. It is soluble in 30 parts of alcohol and 5 parts of hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

I. 0.1839 gram of the salt thus dried gave 0.1416 gram of $BaSO_4$, equal to 0.0194 gram of S or 10.57 per cent.

II. 0.2355 gram of the salt gave 0.1936 gram of $BaSO_4$, equal to 0.0265 gram of S or 10.86 per cent.

	Calculated for $C_{16}H_{15}NO_2S$.	Found. I.	II.
S	10.63	10.57	10.86

Dimethylaniline, $C_6H_5N(CH_3)_2$, *and methyldiphenylamine*, $(C_6H_5)_2NCH_3$, were also treated with benzene-sulphonic acid. In both cases an alcoholic solution of the amine was added to the aqueous solution of the acid, and the alcohol was driven off. Although both united apparently with the acid, still it was impossible to obtain crystalline salts, even by previous concentration to a temperature of 150°. The syrupy products were also kept for some time in a freezing mixture of ice and salt without, however, giving indications of crystallisation.

XXXV.—ON SOME NEW METALLIC SALTS OF BENZENE-SULPHONIC ACID.

By T. H. Norton and T. W. Schmidt.

The following salts were prepared in connection with the general study of the sulphonic acids already mentioned.

The only compounds formed by the union of metallic bases with benzene-sulphonic acid, thus far prepared and analysed, are the barium, copper, zinc, and silver salts. We have increased this number by the addition of the cadmium, manganese, nickel, cobalt, and mercurous salts. The material used in all these preparations was a concentrated solution of barium benzene-sulphonate, obtained as indicated in the early part of the preceding paper.

Cadmium benzene-sulphonate, $(C_6H_5.SO_3)_2 Cd + 7H_2O$.—A concentrated solution of cadmium sulphate was carefully added to the

solution of barium benzene-sulphonate until barium sulphate was no longer precipitated. The filtered solution of cadmium sulphonate was concentrated and allowed to crystallise. This salt crystallises in thin white leaflets containing 7 molecules of water of crystallisation. The water of crystallisation is lost below 100°, the translucent crystals becoming opaque. At 110° they undergo decomposition. They are soluble in two parts of hot water, four and a half parts of cold water, eight parts of alcohol, and twenty-five parts of ether.

Analysis: 1.9677 grams of the salt dried to constant weight at 40°, lost on heating to 100°, 0.4561 gram H_2O, or 23.12 per cent.

	Calculated for $Cd(C_6H_5SO_3)_2 + 7H_2O.$	Found.
H_2O	22.86	23.12

I. 0.3571 gram of the salt dried to constant weight at 100° gave 0.1047 gram of CdO, equal to 0.0917 gram of Cd or 25.75 per cent.

II. 0.4213 gram of the anhydrous salt gave 0.1232 gram of CdO, equal to 0.1078 gram of Cd, or 25.92 per cent.

III. 0.3723 gram of the anhydrous salt gave 0.3946 gram of $BaSO_4$, equal to 0.0542 gram of S or 14.56 per cent.

	Calculated for $CdC_{12}H_{10}S_2O_6.$	Found. I.	Found. II.
Cd	26.29	25.75	25.92
S	15.02	14.56	...

Manganese benzene-sulphonate, $(C_6H_5SO_3)_2Mn + 6H_2O.$—A concentrated solution of manganese sulphate was added to the solution of barium sulphonate to the point of complete precipitation of barium sulphate. On concentrating the filtered solution of manganese sulphonate it was crystallised in the form of thin white scales with a mother of pearl lustre. The crystals contain six molecules of water of crystallisation, which are lost below 100°, when the translucent crystals become opaque. At 130° the salt begins to decompose, turning first gray and then black. The crystals are soluble in 20 parts of ether and six parts of alcohol, while one part of water dissolves four parts of the crystals.

Analysis: 2.9396 grams of the crystals dried to constant weight at 40°, lost on heating to 100°, 0.6532 gram H_2O, equal to 22.24 per cent.

	Calculated for $Mn(C_6H_5SO_3)_2 + 6H_2O.$	Found.
H_2O	22.63	22.24

I. 0.8156 gram of the anhydrous salt dried to constant weight at 100° gave 0.1753 gram of Mn_3O_4, equal to 0.1263 gram Mn or 14.40 per cent.

II. 0.4375 gram of the same substance gave 0.0956 gram of Mn_3O_4, equal to 0.0689 gram Mn or 14.68 per cent.

III. 0.8375 gram of the same gave 1.0035 grams $BaSO_4$, equal to 0.1377 gram S or 16.46 per cent.

IV. 0.8653 gram of the same gave 1.0806 grams $BaSO_4$, equal to 0.1479 gram S or 17.14 per cent.

	Calculated for $Mn(C_6H_5SO_3)_2$.	I.	Found. II.
Mn	14.90	14.40	14.68
S	17.34	16.46	17.14

Nickel benzene-sulphonate, $(C_6H_5SO_3)_2Ni + 6H_2O$.—The preparation was similar to that of the preceding salts, use being made of a concentrated solution of nickel sulphate. Nickel benzene-sulphonate crystallises readily in large well defined octagonal plates, which are colorless by transmitted light, and a delicate green by reflected light. It contains six molecules of water of crystallisation, which are lost at 100°, while at the same time the color becomes a dingy yellow. The anhydrous salt is extremely deliquescent. It decomposes at 165°. It is soluble in two parts of hot water, eight parts of cold water, seventeen parts of alcohol, and twenty-two parts of ether.

Analysis: I. 0.4938 gram of the crystallised salt dried to constant weight at 40°, lost on heating to 100°, 0.1113 gram H_2O, or 22.54 per cent.

II. 0.8573 gram of the same gave 0.1317 gram of NiO, equal to 0.1034 gram Ni or 12.08 per cent.

III. 0.9242 gram of the same gave 0.1488 gram of NiO, equal to 0.117 gram Ni or 12.69 per cent.

IV. 0.4632 gram of the same gave 0.4401 gram of $BaSO_4$, equal to 0.0604 gram S or 13.0 per cent.

V. 1.3825 grams of the same gave 1.2968 grams of $BaSO_4$, equal to 0.1651 gram S or 12.88 per cent.

	Calculated for $Ni(C_6H_5SO_3)_2 + 6H_2O$:	I.	Found. II.
H_2O	22.46	22.54	...
Ni	12.27	12.08	12.69
S	13.30	13 00	12.88

Cobalt benzene-sulphonate, $Co(C_6H_5SO_3)_2 + 6H_2O$.—This salt was prepared in the same way as the preceding compounds, a concentrated solution of cobalt sulphate being used. The crystals are obtained in the form of octagonal plates—thicker than in the case of the nickel salt—colorless by transmitted light, and light red by reflected light. They contain 6 molecules of water of crystallisation, which are lost at 100°, the color at the same time becoming purple. Decomposition takes place at 185°. The crystallised salt dissolves in 3 parts of hot water, 11 parts of cold water, 22 parts of alcohol, and 34 parts of ether. The anhydrous salt is very deliquescent.

Analysis: I. 0.4810 gram of the crystallised salt dried to constant weight at 40°, lost on heating to 100°, 0.1076 gram of H_2O, or 22.20 per cent.

II. 0.7665 gram of the same gave 0.1223 gram of CoO, equal to 0.0961 gram of Co or 12.55 per cent.

III. 0.8511 gram of the same gave 0.1395 gram of CoO, equal to 0.1096 gram of Co or 12.89 per cent.

IV. 1.2995 grams of the same gave 1.1893 grams of $BaSO_4$, equal to 0.1633 gram of S or 12.56 per cent.

V. 1.1205 grams of the same gave 1.0538 grams of $BaSO_4$, equal to 0.1448 gram of S or 12.90 per cent.

	Calculated for $Co(C_6H_5SO_3)_2 + 6H_2O$.	I.	Found. II.
H_2O	22.54	22.20	...
Co	12.27	12.55	12.89
S	13.30	12.56	12.90

Mercurous benzene-sulphonate, $C_6H_5SO_3Hg$.—This salt was precipitated in the form of an amorphous mass on the addition of a solution of mercurous nitrate to a solution of barium benzene-sulphonate. It is anhydrous and of a yellowish white color. It decomposes at 185°, decomposition being indicated by the appearance of small globules of mercury. It is insoluble in water and alcohol, and very slightly soluble in ether.

Analysis: I. 0.443 gram of the salt dried to constant weight at 40° gave 0.2911 gram of HgS, equal to 0.2518 gram of Hg or 56.83 per cent.

II. 0.6266 gram of the same gave 0.4176 gram of HgS, equal to 0.3591 gram of Hg or 56.60 per cent.

III. 1.4031 grams of the same gave 0.8815 gram of $BaSO_4$, equal to 0.1218 gram of S or 8.68 per cent.

IV. 1.5181 grams of the same gave 0.9625 gram of $BaSO_4$, equal to 0.1322 gram of S or 8.70 per cent.

	Calculated for $HgC_6H_5SO_3$.	Found.	
		I.	II.
Hg	56.01	56.83	56.60
S	8.96	8.68	8.70

With regard to the amount of water of crystallisation in the first four salts described, it may be mentioned that with the exception of the cadmium salt, all possess the same number of molecules of water, viz. $6H_2O$, that has been found previously in the copper and zinc salts of benzene-sulphonic acid.

XXXVI.—ON THE AMINE SALTS OF PARA-TOLUENE-SULPHONIC ACID.

By T. H. Norton and A. H. Otten.

The matter contained in this paper was prepared in connection with the general study of sulphonic acids alluded to in the two preceding articles.

The para-toluene-sulphonic acid used in the preparation of the salts to be described was made according to the directions of Chrustschow,[1] viz., by adding concentrated sulphuric acid, drop by drop, to boiling toluene. The best results were obtained by using equal weights of hydrocarbon and acid. The sulphonic acid was purified in the same manner as indicated in paper XXXIV for the preparation of the benzene-sulphonic acid, viz., neutralisation with barium carbonate and careful precipitation of the barium by sulphuric acid.

As the melting point of the crystallised para-toluene-sulphonic acid has not been hitherto ascertained, it was carefully determined and found to be 92°. On adding amines to this acid, as a rule stable salts are formed,most of which are soluble in water. Those obtained from the amines of the aromatic series crystallise easily in well defined forms, while the amines of the normal paraffin series yield salts which,on account of their great solubility,are generally obtained in radial crystalline masses or rosettes. The former class are likewise less soluble in water and more soluble in alcohol than the

[1] Ber. d. chem. Ges. **7**, 1167.

latter. A third difference is noticed in their deportment towards test paper. The former have a pronounced acid reaction, while the latter are neutral or alkaline. All of the salts are, like ammonium para-toluene-sulphonate, destitute of water of crystallisation.

In the determinations of sulphur, Pearson's method (see paper XXXIV) was used exclusively, and with highly satisfactory results.

Methylamine Para-toluene-sulphonate, $C_7H_7SO_3H.NH_2CH_3$.— A 33 per cent. aqueous solution of methyl-amine was added to the concentrated aqueous solution of para-toluene-sulphonic acid. On concentration the salt crystallises in pale rose-colored rosettes which have a mother-of-pearl lustre, are anhydrous, and melt at 125°. The salt is insoluble in carbon disulphide, ether, and benzene. It dissolves in 10 parts of alcohol, $1\frac{1}{2}$ parts of water at 23°, and less than 1 part of water at 100°. It is very deliquescent.

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110°.

I. 0.2334 gram of the salt thus dried gave 0.2639 gram of $BaSO_4$, equal to 0.0362 gram of S or 15.53 per cent.

II. 0.2063 gram of the dried salt gave 0.2361 gram of $BaSO_4$, equal to 0.0324 gram of S or 15.71 per cent.

	Calculated for $C_8H_{13}O_3SN$.	Found. I.	II.
S	15.76	15.53	15.71

Dimethylamine Para-toluene-sulphonate, $C_7H_7SO_3H.NH(CH_3)_2$. —Preparation similar to that of the preceding salt. It crystallises in white fibrous masses with a feathery appearance, is anhydrous, melts at 78°, and is very deliquescent. It is insoluble in carbon disulphide, ether, and benzene. It dissolves in 2 parts of alcohol, and in one part of water at 23°. The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110°.

I. 0.2333 gram of the salt thus dried gave 0.2458 gram of $BaSO_4$, equal to 0.0337 gram of S or 14.46 per cent.

II. 0.2304 gram of the dry salt gave 0.2452 gram of $BaSO_4$, equal to 0.0336 gram of S or 14.61 per cent.

	Calculated for $C_9H_{15}O_3SN$.	Found. I.	II.
S	14.75	14.46	14.61

Trimethylamine Para-toluene-sulphonate, $C_7H_7SO_3H.N(CH_3)_3$. —Preparation similar to that of the preceding salts. It crystallises in pale green rosettes which melt at 92°, are anhydrous,

and are very deliquescent. The crystals are insoluble in carbon disulphide, ether, and benzene. They are soluble in 4.3 parts of alcohol and 3.7 parts of cold water.

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110°.

I. 0.2176 gram of the salt thus dried gave 0.2146 gram of $BaSO_4$, equal to 0.0294 gram of S or 13.54 per cent.

II. 0.2195 gram of the dry salt gave 0.222 gram of $BaSO_4$, equal to 0.0304 gram of S or 13.89 per cent.

	Calculated for $C_{10}H_{17}O_3SN.$	Found. I.	II.
S	13.85	13.54	13.89

Ethylamine Para-toluene-sulphonate, $C_7H_7SO_3H.NH_2C_2H_5.$ — Preparation similar to that of the methyl salts. It crystallises in white radial masses which are anhydrous and very deliquescent. The melting point is 111°. The salt is insoluble in carbon disulphide, ether, and benzene. It is soluble in 7.7 parts of alcohol, in one half its weight of water at 100°, and in less than its weight of water at 23°.

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110°.

I. 0.503 gram of the salt thus dried gave 0.5309 gram of $BaSO_4$, equal to 0.0729 gram of S or 14.49 per cent.

II. 0.3371 gram of the dry salt gave 0.3495 gram of $BaSO_4$, equal to 0.048 gram of S or 14.27 per cent.

	Calculated for $C_9H_{15}O_3SN.$	Found. I.	II.
S	14.75	14.49	14.27

Diethylamine Para-toluene-sulphonate, $C_7H_7SO_3H.NH(C_2H_5)_2.$ —Diethylamine was added to the solution of the sulphonic acid until the liquid was neutralised. On concentration the salt crystallises in white rosettes or warts which are anhydrous and very deliquescent. The melting point is 88°. The crystals are insoluble in carbon disulphide, ether, and benzene. They are soluble in 3.7 parts of alcohol, and in 1 part of water at 23°.

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110°.

I. 0.4423 gram of the salt thus dried gave 0.4157 gram of $BaSO_4$, equal to 0.057 gram of S or 12.89 per cent.

II. 0.372 gram of the dry salt gave 0.3595 gram of $BaSO_4$, equal to 0.0499 gram of S or 13.27 per cent.

	Calculated for $C_{11}H_{19}O_3SN$.	Found. I.	II.
S	13.06	12.89	13.27

Triethylamine Para-toluene-sulphonate, $C_7H_7SO_3H.N(C_2H_5)_3$. —Preparation similar to that of the preceding salt. It crystallises in very deliquescent fibrous white masses. It is anhydrous and melts at 65°. The fused mass becomes green on heating to 110°. The crystals are insoluble in carbon disulphide, ether, and benzene. They dissolve in 2 parts of alcohol and 0.6 parts of water at 22°. The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110°.

I. 0.3531 gram of the salt thus dried gave 0.3087 gram of $BaSO_4$, equal to 0.0424 gram of S or 12.00 per cent.

II. 0.3395 gram of the dry salt gave 0.3007 gram of $BaSO_4$, equal to 0.0412 gram of S or 12.16 per cent.

	Calculated for $C_{13}H_{23}O_3SN$.	Found. I.	II.
S	11.72	12.00	12.16

Aniline Para-toluene-sulphonate, $C_7H_7SO_3H.NH_2C_6H_5$. — This salt was obtained by adding aniline to an alcoholic solution of the sulphonic acid. It forms long glistening white needles which assume a mother-of-pearl lustre on heating to 110°. The crystals are anhydrous, possess an acid reaction, and melt at 223°. They are insoluble in carbon disulphide, ether, and benzene. They dissolve in 5.2 parts of alcohol, 2 parts of water at 100°, and 8 parts of water at 23°.

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110°.

I. 0.3062 gram of the salt thus dried gave 0.2859 gram of $BaSO_4$, equal to 0.0392 gram of S or 12.82 per cent.

II. 0.1815 gram of the dry salt gave 0.1662 gram of $BaSO_4$, equal to 0.0228 gram of S or 12.63 per cent.

	Calculated for $C_{13}H_{15}O_3SN$.	Found. I.	II.
S	13.28	12.82	12.63

Diphenylamine Para-toluene-sulphonate, $C_7H_7SO_3H.NH(C_6H_5)_2$. —Diphenylamine was added to the ethereal solution of the sul-

phonic acid to saturation. The salt crystallises in fine needles of a greenish gray color, which are anhydrous and melt at 64°. The fused salt turns deep green at 225° and decomposes at 255°. The salt is insoluble in carbon disulphide and benzene. It dissolves in 2.5 parts of alcohol and in 31 parts of ether. It is decomposed by water.

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110°.

I. 0.2013 gram of the salt thus dried gave 0.1397 gram of $BaSO_4$, equal to 0.0191 gram of S or 9.53 per cent.

II. 0.2053 gram of the dry salt gave 0.1405 gram of $BaSO_4$, equal to 0.0192 gram of S or 9.39 per cent.

	Calculated for $C_{19}H_{19}O_3SN$.	Found. I.	II.
S	9.38	9.53	9.39

Ortho-toluidine Para-toluene-sulphonate, $C_7H_7SO_3H.NH_2C_7H_7$. —This salt is obtained by adding ortho-toluidine to an alcoholic solution of the sulphonic acid. It crystallises on concentration in long narrow prisms of a light purplish color, which are anhydrous and melt at 180°.

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110°.

I. 0.304 gram of the salt thus dried gave 0.2588 gram of $BaSO_4$, equal to 0.0355 gram of S or 11.69 per cent.

II. 0.3017 gram of the dry salt gave 0.2446 gram of $BaSO_4$, equal to 0.0335 gram of S or 11.13 per cent.

	Calculated for $C_{14}H_{17}O_3SN$.	Found. I.	II.
S	11.47	11.69	11.13

a-Naphthylamine Para-toluene-sulphonate, $C_7H_7SO_3H.NH_2$ $(C_{10}H_7)$.—*a*-Naphthylamine was added to an alcoholic solution of the sulphonic acid. On concentration the salt crystallises in anhydrous needle-like prisms of a grayish color. They turn purplish on heating and melt at 239°. The salt is insoluble in carbon disulphide, benzene, ether, and water, but dissolves in 20 parts of alcohol.

The salt dried over sulphuric acid in vacuo to constant weight lost no weight on heating to 110°.

I. 0.2345 gram of the salt thus dried gave 0.1747 gram of $BaSO_4$, equal to 0.0239 gram of S or 10.23 per cent.

II. 0.2604 gram of the dry salt gave 0.191 gram of $BaSO_4$, equal to 0.0262 gram of S or 10.07 per cent.

	Calculated for $C_{17}H_{17}O_3SN$.	Found. I.	II.
S	10.16	10.23	10.07

Reaction with dimethyl-aniline.—An aqueous solution of para-toluene sulphonic acid was saturated with an alcoholic solution of dimethyl-aniline. The mixture was concentrated on the water-bath, but no crystals appeared. The viscous liquid was then heated to 150° to drive off the last traces of water, and, although it was afterward kept for several days in a freezing mixture, no crystals could be obtained.

SOME HIGHER HOMOLOGUES OF COCAINE.[1]

BY FREDERICK G. NOVY.

The well known alkaloid cocaine is the methyl ester of benzoyl-ecgonine. This latter substance does not occur ready formed in nature, but it is obtained by the saponification of cocaine. The process is one of simple hydration; the alkaloid splitting up into benzoyl-ecgonine and methyl alcohol according to the equation:

$$C_{17}H_{21}NO_4 + HOH = C_{16}H_{19}NO_4 + CH_3OH.$$

On heating benzoyl-ecgonine with methyl iodide and methyl alcohol it is readily converted back into cocaine. Similarly, when heated with any one of the higher alkyl iodides the corresponding homologue of cocaine is obtained.

The ethyl ester of benzoyl-ecgonine was first prepared and partially studied by W. Merck in 1885. He obtained it by heating benzoyl-ecgonine with ethyl iodide and ethyl alcohol in a sealed tube for 8 hours at 100°. This method with slight modifications was the one used in the preparation of this and the succeeding homologues. Several grams of benzoyl-ecgonine were heated about 5 hours at 95° with a quantity of ethyl iodide slightly in

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[1] Read at the New York meeting of the American Association for the Advancement of Science.

excess of the theoretically required amount, and some absolute alcohol. When cold the tube was opened and the contents transferred to a small evaporating dish. The alcohol and excess of ethyl iodide was driven off at a low heat on the water-bath. The yellowish syrup was taken up with warm water, filtered, and the filtrate after being made alkaline with sodium carbonate was extracted with ether. The ether solution on evaporation left a yellowish crystalline mass. This was further purified by dissolving it in dilute hydrochloric acid; the acid solution was filtered, and the filtrate extracted repeatedly with ether to remove the coloring matter. The colorless solution thus obtained was now made alkaline with sodium carbonate and again extracted with ether. On evaporation of the ether solution the alkaloid was obtained in the form of delicate white silky crystals, arranged in sheaves or stellate groups. By recrystallisation from alcohol the substance was obtained in large clear monoclinic prisms resembling those of cocaine. Analysis of the platinum salt gave results agreeing with the formula $[C_{16}H_{18}(C_2H_5)NO_4.HCl]_2PtCl_4$.

Ladenburg has suggested for this compound the name cocethyline. And according to this nomenclature the next higher member would be cocpropyline, etc. I have preferred to use names which suggest the chemical constitution of the substance. Thus, since cocaine is the methyl ester of benzoyl-ecgonine, it can be named *methyl-benzoyl-ecgonine.* The succeeding homologues accordingly become *ethyl-benzoyl-ecgonine, propyl-benzoyl-ecgonine*, etc.

The crystals of ethyl-benzoyl-ecgonine melt at $107°-108°$, and solidify again at about $90°$. Like cocaine it forms easily crystallisable salts. The hydrochloride crystallises in beautiful colorless needles or prisms. It is readily soluble in water and alcohol, insoluble in ether. Platinum chloride produces in solutions of the hydrochloride a yellow precipitate of splendid glittering rhombic plates. The precipitate is soluble in warm water, from which it recrystallises on cooling. It is also soluble in hydrochloric acid and in warm alcohol.

Gold chloride produces a voluminous yellowish-white precipitate, soluble in warm water, in excess of cold hydrochloric acid, and in alcohol. Phospho-molybdic acid gives a heavy yellowish-white precipitate. Mayer's reagent produces a white precipitate ; picric acid, a yellow, readily soluble precipitate ; iodine in potassium iodide yields a kermes-brown precipitate; bromine water, a yellow

precipitate soluble in ammonium hydrate; potassium iodide and potassium sulphocyanide produce only a slight cloudiness; mercuric chloride gives a white precipitate which is readily soluble in warm water; stannous chloride also gives a white precipitate; disodic hydric phosphate produces in concentrated solutions a white precipitate which is soluble in water and in acetic acid.

Hydrobromic acid, iodic acid, ammonium oxalate, ferric chloride, potassic bichromate, give no precipitate; alkalies and alkali carbonates yield a white precipitate which is soluble in large excess.

The alkaloid, as well as its salts, possesses a strong anaesthetic action similar to that of cocaine.

Monobrom-ethyl-benzoyl-ecgonine, $C_{16}H_{18}(C_2H_4Br)NO_4$. — This compound was prepared by heating benzoyl-ecgonine with ethylene bromide and alcohol in a sealed tube for 5 hours at 95°. As in the preparation of the preceding compound the solution was evaporated on the water-bath to drive off the excess of alcohol and ethylene bromide. The syrupy residue was then taken up with water, and after being made alkaline with sodium carbonate was extracted with ether. This on evaporation gave a clear colorless syrup which did not show any sign of crystallisation even after several days.

The free alkaloid, as well as the hydrochloride, has a bitter taste and a strong anaesthetic action. The hydrochloride formed a thick yellowish syrup which showed no tendency to crystallise. When kept for some months over sulphuric acid it solidified to a hard transparent glassy mass, full of cracks but entirely free from crystals. It is readily soluble in water and alcohol, insoluble in ether. Its behavior to reagents is almost identical with that of ethyl-benzoyl-ecgonine.

Propyl-benzoyl-ecgonine, $C_{16}H_{18}(C_3H_7)NO_4$.—This compound was obtained in exactly the same way as the preceding. The benzoyl-ecgonine was heated with propyl iodide and propyl alcohol. The free alkaloid crystallises from ether in fine colorless prisms or radiating silky needles; from alcohol in large transparent flat prisms which melt at 78°–79.5°, and solidify again at about 65°. The low melting point of this compound and of the following isobutyl derivative deserves special attention. Benzoyl-ecgonine containing four molecules of water melts at 90°–92°, while cocaine, the methyl derivative, melts at 98°, and the ethyl compound has its melting point at 107°–108°. Although

the propyl and isobutyl compounds were repeatedly prepared, the melting points were found to be always constant and lower than those of the other homologues. This is perhaps due to a different position of the substituting group in the molecule.

The alkaloid has a very bitter taste and possesses a strong anaesthetic action. The hydrochloride is readily soluble in water and alcohol, insoluble in ether. Ordinarily it is in a syrupy condition, but when kept over sulphuric acid for some time it yields a mass of fine white crystals. With reagents it behaves the same as the preceding.

Disodic hydric phosphate produces in concentrated solutions a white precipitate which is at first amorphous, but soon crystallises, forming long colorless plates often arranged in groups. They are soluble in water and in acetic acid.

Isobutyl-benzoyl-ecgonine, $C_{16}H_{18}(C_4H_9)NO_4$.—The same method of preparation was used for this compound as for the preceding; isobutyl iodide and the corresponding alcohol being employed. The ether solution of the alkaloid on evaporation left a colorless syrup which soon began to crystallise. Recrystallised from alcohol it gave a mass of short colorless prisms which melted at 61°–62°. They possess an intense bitter taste and strong anaesthetic action.

The hydrochloride solidifies over sulphuric acid to a hard yellowish glassy mass almost free from crystals. It exhibits the same reactions with reagents as cocaine and the other homologues. Potassium iodide and sulphocyanide produce in concentrated solutions a white precipitate.

ON THE SUPPOSED DISSOCIATION OF ZINC OXIDE,
And the Condition of the Atmosphere within a Platinum Vessel Heated by a Gas Flame.

By H. N. Morse and W. M. Burton.

Some years ago it was found by one of us that zinc, in the highest state of purity and in considerable quantity, can be prepared by subjecting the metal to fractional distillation in a vacuum.

When the pressure is wholly removed the zinc distills at a temperature apparently not much above its fusing point, while the other metals usually associated with it are, at that temperature, very much more or very much less volatile. The separation of zinc from lead by this method is especially rapid and satisfactory. It seemed desirable, therefore, that a redetermination of the atomic weight of the metal, with the elementary substance as a starting point, should be undertaken.

Of all the methods which have been employed for the purpose, or which suggested themselves as feasible, the determination by means of the oxide appeared to be the most simple and direct, and therefore the best, provided the stability of the oxide at high temperatures could be demonstrated. The details of our work will be published at a later date; but some of the results having a more general interest, we venture to present them now. Having demonstrated that the oxide of zinc does not lose weight when heated for many hours in the muffle furnace to a temperature above that required to fuse steel; moreover, that the platinum crucibles containing the oxide do not exhibit any trace of tarnish after such heating; we turned our attention to a phenomenon which must be familiar to many chemists, namely, that when the oxide of zinc is heated in platinum over a blast lamp, or even over an efficient simple burner without blast, it constantly loses weight.

Axel Erdmann[1] observed, while making a determination of the atomic weight of zinc, that when the oxide is heated in a crucible the platinum becomes coated with a blue tarnish supposed to be an alloy of zinc and platinum. Much later Marignac[2] noticed the same tarnish upon the platinum when the oxide is heated over the blast lamp; moreover, that there is a manifest distillation of the zinc out of the crucible and a constant loss in weight. This loss he ascribes to *dissociation* of the oxide.

In view of the results of Deville[3] relating to the dissociation temperature of water, and of Deville and Troost[4] relating to the permeability at high temperatures of platinum to hydrogen, it appeared probable to us that the phenomenon is one of *reduction* and not of *dissociation;* that the temperature of the gas flame in parts being above that at which the dissociation of water begins, there is in the flame at the same time free oxygen and free hydro-

[1] Ann. Chem. (Liebig), **50**, 438.   [2] Archives des Sciences Phys. et Nat. (3) **10**, 193.
[3] Jsb. Chem. 1860, 24.   [4] Jsb. Chem. 1863, 23.

gen resulting from the dissociation of water previously formed by the combustion of the gas. The result would be an accumulation of free hydrogen on the inside of any platinum vessel heated in the gas flame, due to the more rapid diffusion of hydrogen through heated platinum. Our results have justified this explanation, and make it appear probable that the atmosphere within a platinum vessel heated by such flames as are employed in the laboratory is always a *reducing* atmosphere.
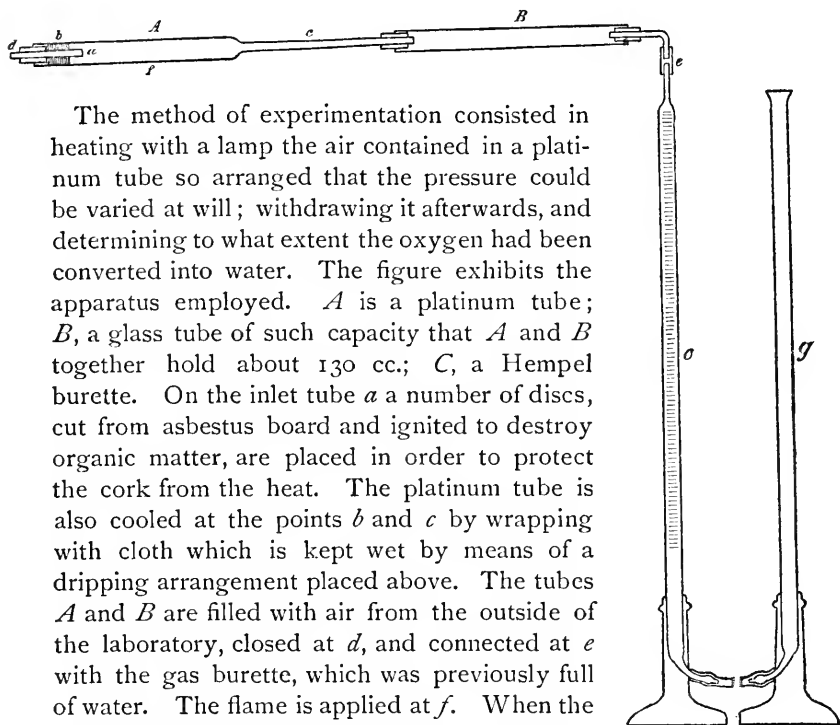
The method of experimentation consisted in heating with a lamp the air contained in a platinum tube so arranged that the pressure could be varied at will; withdrawing it afterwards, and determining to what extent the oxygen had been converted into water. The figure exhibits the apparatus employed. A is a platinum tube; B, a glass tube of such capacity that A and B together hold about 130 cc.; C, a Hempel burette. On the inlet tube a a number of discs, cut from asbestos board and ignited to destroy organic matter, are placed in order to protect the cork from the heat. The platinum tube is also cooled at the points b and c by wrapping with cloth which is kept wet by means of a dripping arrangement placed above. The tubes A and B are filled with air from the outside of the laboratory, closed at d, and connected at e with the gas burette, which was previously full of water. The flame is applied at f. When the air within the tubes has attained its maximum expansion, the level of the water in g is adjusted according to the pressure which it is desired to maintain in the apparatus. At the end of each ten minute period of heating the tube is allowed to cool down, in order to facilitate the mixing of the portions of the gas in A, B and C. Finally a small glass tube, filled with water and dipping under water in a beaker, is attached at d; the gas withdrawn by lowering g, and analysed by the method of Hempel.

The substances looked for, and determined when found, were carbon dioxide, oxygen, carbon monoxide, hydrogen, and nitrogen.

The quantity of carbon dioxide found was not in any case in excess of the quantity normally contained in the air, and was, of course, hardly measurable in the ordinary Hempel burette. Carbon monoxide was not found at all. The hydrogen was determined by absorption in palladium sponge, the tube containing it having first been filled with pure nitrogen. The fact that the air did not perceptibly diminish in volume when treated with caustic potassa to withdraw carbon dioxide, proves that no oxides of nitrogen were formed during the heating. Great care was taken in all cases to use only an oxidising flame, and not to allow the internal cone containing the unburned gases to come in contact with the platinum tube. The results obtained are stated in · Table I. The percentages of oxygen given represent the proportion of that element which *disappeared* during the heating, and are calculated on the basis that the air contains 20.9 per cent. of oxygen and 79.1 per cent. of nitrogen. The quantities of free hydrogen found are given in cubic centimetres.

TABLE I.

No. of Exp.	Source of Heat.	Time of Heating.	Pressure.	Percent. of total oxygen lost.	Cc. free Hydrogen found.
1	Blast Lamp.	1 Hour.	Atmos. Press. less 30 mm. Merc.	63.07	
2	"	1 "	"	62.08	
3	"	1 "	Atmos. Press.	53.70	
4	"	1 "	"	54.13	
5	"	1 "	At. Pr. + 30 mm. Merc.	48.67	
6	"	2 "	At. Press.	88.49	
7	"	2 "	"	88.53	
8	"	3 "	"	98.14	2.4
9	"	4 "	"	100.00	2.7
10	Simple Bun-	3 "	"	55.56	
11	sen Burner	6 "	"	81.81	
12	without Blast.	10 "	"	97.00	0.7

In Table II are given the number of cubic centimetres of oxygen burned out in each experiment, also the minimum volume of free hydrogen which must have diffused from the flame into the tube. The calculation is, of course, based on the supposition that the

residual nitrogen is to the oxygen originally mingled with it as 79.1 is to 20.9.

TABLE II.

No. of Exp.	Vol. of O_2 lost.	Min. vol. of H_2.
I	13.75 CC	27.50 CC
2	14.89	29.78
3	11.40	22.80
4	11.41	22.82
5	10.43	20.86
6	21.73	43.46
7	22.28	44.56
8	21.03	$\left.\begin{matrix} 2.4 \\ 42.06 \end{matrix}\right\} 44.46$
9	22.75	$\left.\begin{matrix} 2.70 \\ 45.50 \end{matrix}\right\} 48.20$
10	12.50	25.00
11	19.80	39.60
12	22.81	$\left.\begin{matrix} 0.70 \\ 45.62 \end{matrix}\right\} 46.32$

If we compare the results of Experiments Nos. 1 and 2 with 3 and 4, and with 5, it appears that the diffusion of hydrogen from the flame through platinum is affected by difference in pressure, being greater when the pressure on the inside is diminished. It appears from Experiments Nos. 8 and 12 that when the oxygen has been reduced to a small quantity, both free oxygen and free hydrogen may exist together in the tube.

Experiment No. 9 was undertaken in order to determine whether it is possible wholly to remove the oxygen, and the fact that the volume did not perceptibly decrease when the gas was passed into the phosphorus absorption pipette indicates that it may. But the gas, when it was returned to the burette for measurement, appeared to contain a minute quantity of the white clouds which appear when oxygen is absorbed by phosphorus. To settle this question satisfactorily, finer measuring apparatus and greater precautions against possible diffusion of oxygen from the outside will be required.

That the quantity of free hydrogen found in Experiment No. 9 was not markedly larger than that found in No. 8 is not surprising, because, the tube being hot on all sides, it passes out of the rear wall with nearly the same facility that it enters in front. Moreover,

the connections are necessarily such that free hydrogen would be lost through them. It was our first plan to fill the tube with some gas free from oxygen, and to measure the hydrogen which accumulated in it; but the reflection that free hydrogen was not likely under the circumstances to accumulate with rapidity, and that the quantity found afterwards would be no measure of that which had diffused in during the experiment, led us to select air instead.

Our results appear to explain sufficiently the cause of the constant loss in weight when the oxide of zinc is heated in platinum over a gas flame, and to make it extremely probable that the atmosphere within any platinum vessel heated by any gas flame whatever will receive free hydrogen. They also explain the origin of many of those tarnishes and sublimates which the analytical chemist so often finds on the inside of his crucible after heating substances supposed to be non-volatile. Since only the so-called oxidising portions of the flames were allowed to come in contact with the platinum, the free hydrogen which diffused through the metal must have been produced by the dissociation of water. Whether this dissociation is due solely to the high temperature of the flame, or in part to the influence of the platinum itself, is a question for further investigation. It appears not improbable that the very different rates of diffusion of hydrogen and oxygen through platinum at high temperatures may be a cause of the dissociation of the highly heated water vapor, just as different rates of diffusion through liquids of the constituents of some compounds may determine their decomposition while undergoing solution.

The idea suggests itself in this connection that the oxidising effect of the outer blow-pipe flame may be due to the oxygen derived from dissociating water, rather than from the excess of oxygen blown into it. Such a supposition accords well with the common experience that the best oxidising effects are produced by the *hottest* flame, and not by the flame into which a large excess of air is pumped. A molecule of water heated to a temperature at which it becomes unstable would doubtless be a more active oxidising agent than a molecule of free oxygen.

Chemical Laboratory, Johns Hopkins University.

A METHOD FOR THE SEPARATION AND DETERMINATION OF BORIC ACID.

By H. N. MORSE AND W. M. BURTON.

The indicator, tropaeolin *OO*, not being sensitive to boric, carbonic, and silicic acids, or to their salts, it is practicable to liberate exactly one or all of these acids in any mixture of inorganic substances. In other words, if to a solution containing silicates, carbonates, and borates, and any other inorganic salts or hydroxides, we add tropaeolin and then dilute sulphuric acid, we shall not obtain an acid reaction until all of the silicic, carbonic, and boric acids have been liberated. In the meantime, any oxides or hydroxides which were present will have been converted into sulphates, so that the mixture will finally consist of neutral salts, water, silicic, carbonic, and boric acids. If we now add to this mixture a sufficient quantity of dehydrated copper sulphate, the water will be absorbed and the silicic acid dehydrated. The mass will then consist of neutral salts, silica, and boric acid, of which only the boric acid is soluble in absolute alcohol. These facts enable us to separate boric acid with great exactness from nearly all other forms of inorganic matter. The only classes of salts known to us at present which are at all likely to interfere with such a separation, are the chlorides and the compounds of iron, but both of these may be readily removed before the acids in question are liberated. The boric acid thus separated may be determined as a meta-borate of calcium, magnesium, or barium. We prefer the last form ; because a mixture of carbonate and meta-borate of barium, being neither markedly hygroscopic nor capable of absorbing carbon dioxide, can be brought to a constant weight more readily than one containing the oxide of calcium or magnesium. Moreover, the use of barium enables us to employ a standard solution of hydroxide to receive the alcoholic extract of boric acid, thus saving the labor of bringing the absorbing material itself to a constant weight.

The Reagents.

1. An aqueous solution of tropaeolin *OO*.

2. A standard solution of sulphuric acid of such strength that one cubic centimeter of it is equivalent to twenty milligrams of barium carbonate.

3. A solution of barium hydroxide approximately equivalent to the sulphuric acid. This is prepared by agitating the solid commercial hydroxide with a little cold water, filtering, and washing with cold water. The residue, thus freed from the caustic alkalies, is transferred to a flask or bottle and treated with water. From this solution the more dilute ones are prepared as they are needed.

4. Dehydrated copper sulphate prepared from the pure salt by heating in an air-bath at 150° until the whole mass assumes a uniform light color. It is necessary to use pure copper sulphate for this purpose. The presence either of chlorides or of iron salts is not permissible, because of the solubility of cupric chloride and ferric sulphate in alcohol. It is not advisable to attempt to remove more than four of the five molecules of water of crystallisation, because of the danger of decomposing some of the salt at high temperatures. Such decomposition would result in the formation of free sulphuric acid, which would be extracted along with the boric acid by alcohol.

5. Absolute alcohol prepared by digesting for two or three days with dehydrated copper sulphate an alcohol which has previously been distilled over lime. The complete drying of the alcohol is important.

The Mode of Procedure.

If the boric acid is in solution, the liquid containing it is made slightly alkaline with caustic potassa, and evaporated on a water-bath in a porcelain dish having a width of about 100 millimeters. The volume of the solution should be reduced to 10 or 12 cubic centimeters. The separation of salts during evaporation will not interfere with subsequent operations. If the material containing the boric acid is not soluble in water, a silicate for example, a solution is effected by the method recommended by one of us for the decomposition of chrome iron.[1] About four grams of the purest solid potassium hydroxide are placed in a nickel crucible[2] and heated with a small flame until the fused mass becomes perfectly tranquil. The crucible is allowed to cool and the finely ground and weighed material spread over the surface of the solidified hydroxide. The whole is then heated for two hours to a temperature just sufficient to keep the hydroxide in a fused condition.

[1] This Journal **3**, 163.
[2] A silver crucible is not to be recommended, because of the solubility of silver in potassium hydroxide.

During the decomposition the mass is frequently stirred with a stout platinum wire, which is allowed to remain in the crucible. This method of bringing the acid into a soluble condition is to be preferred to fusion with the alkaline carbonates, since it yields a mass from which everything soluble can be readily extracted by water. The crucible is placed on its side in a porcelain dish, treated with hot water, and the soluble separated from the insoluble matter by filtration and washing. The filtrate is then evaporated to the small volume previously mentioned. If the material thus decomposed contains iron, the contents of the crucible must be treated with not less than 400 cubic centimeters of water, and the dish in which the solution is made should be heated on the water-bath for a considerable time, with replacement from time to time of the evaporated water. Otherwise the separation of the iron may not be complete.

The solution of borate is treated, under proper covering to prevent loss by spattering, with a drop or two of tropaeolin solution, and then with the ordinary desk solution of sulphuric acid until a distinct and permanent acid reaction is obtained. The material on the under side of the cover is washed back into the dish with the least possible amount of water, and the slight excess of sulphuric acid carefully neutralised by means of very dilute caustic potassa. The solution of boric acid, which should not exceed 20 cubic centimeters in volume, is now thoroughly dried by slowly stirring into it the anhydrous copper sulphate, care being taken not to permit any considerable rise in temperature. The mass is afterwards pulverised with a pestle.

The extraction apparatus consists of a narrow Erlenmeyer flask having a capacity of about 150 cubic centimeters, and a straight chloride of calcium tube somewhat larger than is necessary to contain the mixture which is to be extracted. The narrow portion of the tube is plugged with cotton wool. To its lower end is attached, by means of rubber tubing, a small glass tube which reaches to the bottom of the flask when the stopper carrying the extraction tube is in position. The quantity of the dilute barium hydroxide solution which is equivalent to 25 cubic centimeters of the standard sulphuric acid, is run into the flask and the apparatus attached to the filter pump. This quantity of the hydroxide would weigh, if converted into carbonate, just 500 milligrams. During the filling of the extraction tube with the copper sulphate mixture,

the outside is occasionally tapped to render the material more compact.

The porcelain dish is washed with several small portions of absolute alcohol, which are then poured into the tube. When the whole of the copper sulphate has become wet with the alcohol the pump is shut off and the mass allowed to soak for fifteen minutes. Afterwards five other portions of absolute alcohol, of 15 cubic centimeters each, are poured into and slowly drawn through the tube, care being taken to allow each portion to filter through completely before another is added.

Finally, the excess of the barium hydroxide is precipitated by passing into it a current of carbon dioxide; the contents of the flask are transferred to a weighed platinum dish, evaporated to dryness, and heated to constant weight over a triple burner.

The quantity of boric anhydride is found by the following proportion:

Mol. weight of B_2O_3—mol. weight of CO_2 : mol. weight of B_2O_3 :: weight found—theoretical weight of the barium as carbonate : weight of B_2O_3 found.

If the atomic weights of Clarke have been used throughout, the difference between the weight found and the calculated weight of the carbonate (500 milligrams) is to be multiplied by the number 2.697012; if those of Meyer and Seubert have been employed, this difference is to be multiplied by the number 2.701822.

The accuracy of the method was tested by determining the boric acid in pure borax glass (prepared by ourselves), in datholite from Bergen Hill, and in tourmaline from Pierrepont, N. Y.

We give the results below:

I. *Borax Glass.*

Measured portions of a standard solution were employed.

Theoretical percentage of B_2O_3, 34.61. Found, 34.64, 34.58, 34.64, 34.57, 34.57.

Five determinations made by Mr. R. L. Henderson of this laboratory gave the following percentages of B_2O_3 in our borax glass, 34.60, 34.60, 34.59, 34.58, 34.59.

II. *Datholite from Bergen Hill.*

Theoretical percentage of B_2O_3, 21.82. Found, 21.75, 21.68, 21.62, 21.65, 21.64. Mean, 21.67.

III. *Tourmaline from Pierrepont.*

This mineral was recently carefully analysed by Dr. Riggs.[1]

Five determinations of the boric acid were made by ourselves, one by Mr. C. C. Blackshear and one by Mr. Henderson.

Percentage of B_2O_3 found by Dr. Riggs, 10.15, 10.00, 10.31; by ourselves, 10.03, 10.08, 10.11, 10.03, 10.13. Mean, 10.08. Found by Mr. Blackshear, 10.02; by Mr. Henderson, 10.12.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

PRELIMINARY NOTE ON THE CONSTITUTION OF SODIUM ACETACETIC AND MALONIC ETHERS.

BY ARTHUR MICHAEL.

In the continuation of an investigation on the constitution of the sodium derivatives of acetacetic and malonic ethers, several observations were recently made that seem of sufficient importance to publish before the completion of the research.

The so-called acetyl-malonic ether was first made by Ehrlich and Conrad and Guthzeit, by the action of chlorcarbonic ether on sodium acetacetic ether; and lately, Lange has published a method for obtaining the substance from acetyl chloride and sodium malonic ether. It is theoretically very probable that the introduction of a negative group like carbethoxyl into acetacetic ether should increase the acid properties; but, to judge from the account Conrad and Guthzeit give of the substance, it hardly seems to be the case. This anomalous behavior of acetyl-malonic ether appeared to me to be a clue that might throw light on the much discussed question of the constitution of sodium acetacetic ether, and led me to re-investigate the subject. I find that the compound obtained from chlorcarbonic ether and sodium acetacetic ether is an entirely different substance from that obtained from acetyl chloride and sodium malonic ether. The first named substance is insoluble, and is not decomposed in the cold by strong alkaline solutions, and dissolves gradually in dilute alkalies under decomposition into acetone, alcohol, and carbonates. It can be recon-

verted into acetacetic ether by means of sodium ethylate, but in this reaction a sodium product is not formed. Acetyl chloride and sodium malonic ether react to form two products, which were separated by fractionation in vacuum. They proved to be mono- and diacetyl malonic ethers. The mono-derivative boils in vacuum five degrees lower than its isomer obtained from acetacetic ether under the same conditions, and acts as a strong acid. It dissolves immediately in strong or dilute alkaline solutions, and even in solutions of alkaline carbonates, and is precipitated unchanged by addition of a mineral acid. Added to an alcoholic sodium ethylate solution, the white crystalline sodium derivative is immediately deposited.

In view of these remarkable results it seemed of interest to re-examine the action of chlorcarbonic ether on sodium malonic ether, as the methinyl-tricarboxylic ether of Conrad and Guthzeit does not form a sodium derivative, but is immediately decomposed by alcoholic sodium ethylate with the formation of sodium carbon-ate. These chemists employed a sodium malonic ether obtained by precipitating its alcohol solution with ether and drying in a vacuum, and then boiled the salt with a solution of chlorcarbonic ether in benzene. In my experiments the sodium derivative was made by the action of sodium on a dilute ethereal solution of malonic ether, and chlorcarbonic ether was added directly to the product. The substance obtained in this manner agrees in its physical properties very closely with those of the substance described by Conrad and Guthzeit, but differs materially from it in its chemical properties. It dissolves immediately in solutions of alkalies or alkali carbonates, and is precipitated unchanged by addition of a mineral acid ; and the stable sodium derivative is formed at once when it comes in contact with alcoholic sodium ethylate.

The results with acetyl malonic ether seem to me to admit of but one plausible interpretation, namely, that sodium acetacetic ether has the constitution $CH_3 — CONa — CH — COOC_2H_5$, although the free ether is undoubtedly represented by $CH_3 —CO — CH_2 — COOC_2H_5$. The product from chlorcarbonic and sodium acetacetic ethers is $CH_3 —COCOOC_2H_5 — CH — COOC_2H_5$, a view that explains the neutral properties and the products of decomposition by alkalies ; while the substance from malonic ether is the real acetyl-malonic ether, and its constitution is therefore $CH_3 — CO — CH(COOC_2H_5)_2$. The differences in the properties

of the methinyl-tricarboxylic ether of Conrad and Guthzeit, and the ether obtained by me, indicate that when sodium replaces hydrogen in malonic ether, the first phase of the reaction is the formation of $CHNa(COOC_2H_5)_2$; but, on heating, owing to the affinity of oxygen for sodium, this product passes over into the more stable form $C\!\!<^{OC_2H_5}_{ONa} - CH - COOC_2H_5$. According to this view, the ether of Conrad and Guthzeit is $C\!\!<^{OC_2H_5}_{OCOOC_2H_5} - CH - COOC_2H_5$, and my substance—it being made at a lower temperature—is the real methinyl-tricarboxylic ether, $CH(COOC_2H_5)_3$. Indeed, it is not improbable that in the replacement of hydrogen of acetacetic ether by sodium, the compound first formed is $CH_3 - CO - CHNa - COOC_2H_5$, but in this case a molecular rearrangement takes place at ordinary temperature, a view for which I shall endeavor to furnish an experimental basis.

These experiments appear to me to open a wide field of discussion in regard to chemical reactions by substitution, and intermolecular changes due to the introduction of positive or negative radicals, that in the present note I can barely touch, but I shall return to the subject when the research is completed and published in full. The formation of homologues of higher carbon series by the action of alkyl haloids on sodium acetacetic ether must be explained by assuming an addition of the alkyl haloid to the sodium derivative and subsequent elimination of sodium haloid. How many of the so-called substitutions are in reality of a similar duplex nature? It can hardly be doubted that many of them represent but the final stage of an addition and subsequent elimination; a view that at least explains many facts at present difficultly or wholly unintelligible. Nor can it be doubted that cases similar to that described with acetacetic ether are uncommon, when hydrogen of an organic substance containing oxygen is replaced by a strongly positive atom. As an example, isatine may be mentioned, whose sodium derivative, according to this view, has the constitution $C_6H_4\!\!<^{N}_{CO}\!\!>CONa$, while the substance itself is represented by $C_6H_4\!\!<^{NH}_{CO}\!\!>CO$; an interpretation explaining the results obtained by v. Baeyer without the need of his pseudoform hypothesis.

TUFTS COLLEGE, MASS.

REVIEWS AND REPORTS.

Etudes de Dynamique Chimique. Par J. H. van't Hoff. Amsterdam, 1884.

This book is so deserving of careful study and has apparently attracted so little attention in this country that a brief notice of it may not be out of place even now, more than three years after its publication. It is composed of an introductory chapter, a list of exact definitions of terms used, and four parts headed as follows: "The March of Chemical Transformation," "The Influence of Temperature," "Chemical Equilibrium," and "Affinity." Each of these parts is in turn subdivided into several heads.

In the introductory chapter the author calls attention to the broad generalisations reached by a study of physical constants as functions of chemical composition, and the far more limited applicability of results attained by a study of chemical action as a function of composition, taking as examples Brühl's and Menschutkin's work ; and as results obtained by work similar to that of the latter chemist are not capable of general application on account of unknown factors due to secondary action and disturbing influence, he points out that the desired simple mathematical expression can be deduced only after a careful study of the "march of chemical transformation" step by step in such a way as to estimate and eliminate each disturbing factor. A large portion of the book is therefore devoted to a study of disturbing influences and methods of eliminating them. In the first part of the book it is shown that if but a single molecule reacts, as for example

$$NH_4Cl = NH_3 + HCl,$$

the amount of change in unit time depends entirely on the quantity of the compound and the coefficient of velocity of the reaction. If more than one molecule reacts, for example,

$$Cl_2 + H_2 = 2HCl,$$
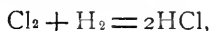
other factors, such as dilution, must be taken into consideration, and the equation used to determine the coefficient of velocity must differ from that used if the reaction be unimolecular. This equation has been given a general form in which n represents the number of molecules that react, and if we have a reaction in which this number is unknown it becomes easy, if we can eliminate disturbing influences, to determine it from this formula. The disturbing influences known to exist are those exerted by the volume occupied by the reacting system, by changes in the medium or solvent brought about by the products of the reaction, by deposition of these products on the walls of the vessels, by the

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shape and size of the vessels, and by atomic movements. The influence of volume may be eliminated by diluting the solution so that the volume occupied by a quantity of solution containing x of the substance is not less than the volume of x in the gaseous state. The influence exerted by the change in the menstruum may be determined by using solutions of different strengths and comparing their rate of change with that of solutions of the same strengths containing the products of the reaction. By moistening the walls of the vessels, and by selecting apparatus of proper shape and size, we can dispose of the third and fourth factors. The influence of atomic motion, which is exhibited by the peculiar behavior of some gases at a particular tension, may be eliminated by the use of a proper diluent. Each of these elements has been carefully studied by van't Hoff, and this portion of the book is particularly interesting. Contact action, induction, and the isomerism of maleic and fumaric acids have also been studied in detail by the author and the results of his work given.

The part entitled " The Influence of Temperature " shows a happy combination of experiment and of theoretical conceptions founded on the principles of thermodynamics. The formulæ deduced from theory and from experiment are found to agree remarkably well. A special chapter is devoted to a consideration of the temperature of ignition, which is defined as " that temperature at which the heat conducted away exactly equals that produced by chemical action."

In the chapters on " Chemical Equilibrium " van't Hoff makes use of the expression $xy \gtreqless x + y$ to indicate that the reactions expressed by $xy = x + y$ and $x + y = xy$ occur simultaneously, and that equilibrium is established when equal amounts of xy and $x + y$ are formed in equal times. He compares chemical equilibrium with physical, and divides it into three forms : homogeneous, in which all the substances are either gaseous or liquid ; heterogeneous, in which they are not all in the same physical state ; and condensed, in which they are solid. He compares the first form ($N_2O_4 \gtreqless 2NO$) with the deviations from the law of Boyle ; the second ($NH_5S \gtreqless NH_3 + H_2S$) with the state of equilibrium represented by a liquid in contact with its vapor ; and the third (orthorhombic sulphur $\gtreqless$ monoclinic sulphur) with a solid in contact with a liquid of the same composition (ice and water). The temperature at which the two condensed systems are in equilibrium, i. e. the temperature at which there is no apparent change in either system, is shown theoretically to be that at which the tension of their vapor is identical. In order still further to test the comparison, the effect of pressure on the temperature of transition of sulphur from the one form to the other was determined experimentally and found to agree perfectly with that calculated from the formula of the effect of pressure on the temperature of fusion. The conclusion reached by a mathematical study of the results obtained

by comparing physical and chemical equilibrium is, that if the state of equilibrium between two systems be changed by lowering the temperature, there is an increase in the amount of that system whose formation from the other is attended with the evolution of heat. From this it can be shown that while the so-called laws of Thomsen and Berthelot regarding maximum heat and maximum work hold good, in general, at ordinary temperatures, they are not true at high, nor are they laws even at ordinary temperatures, but only at absolute zero.

The chapters on " Affinity " deal with some very ingenious experiments upon measuring the attraction of solutions of salts for water and of salts for their water of crystallisation, and the work done in reactions which may be reversed by a change of temperature. That point at which the reaction is reversed is called the point of transition. It was found that the work performed in a chemical reaction depends on the heat evolved, the temperature of the point of transition, and the temperature at which the reaction takes place. A simple mathematical expression for this was deduced, and several interesting applications of this formula are pointed out in the book. F. L.

Sur la Constitution de la Naphtaline et de ses Dérivés. By F. Reverdin and E. Nœlting. Reprinted from the " Bulletin de la Société industrielle de Mulhouse," pp. 76, with twenty extensive tables. 8vo, paper, 6 marks. Mulhouse, Alsace : Veuve Bader & Cie., Printers and Editors.

In one of the early pages the authors use these words, which give a good idea of the scope of the book :

" The work which to-day we have the honor of presenting to you, and which shows the actual state of our knowledge of the naphthalene derivatives, is, for the most part, entirely new, having retained merely the general arrangement of material peculiar to our earlier work.

" We shall discuss at the outset the constitution of naphthalene, the number of its isomeric derivatives, and the methods for the determination of the chemical position. Further on we give, in the form of a series of tables, all the known derivatives, indicating in a few words the preparation, and giving the bibliography complete. With this arrangement it will be easy for any one who may wish to make a thorough study of certain classes of derivatives to refer directly, without loss of time, to the original memoirs. In many cases, from the preparation of a derivative we are already in a position to draw conclusions relative to its constitution, while in other cases its transformation into a derivative of known constitution serves to establish the same. In many cases the structure has not yet been determined with perfect precision, or may even be altogether doubtful. Where this is so, and in general where it appears

to us advantageous, we shall discuss the formulæ in notes annexed to each table."

Coming as this work does from the hands of those who not only occupy prominent places among the leaders in pure chemical research at the present time in Europe, but who at the same time, from their familiarity with the applications of the results of this research in the chemical industry, are able to speak with authority with reference to both sides of the subject, practical as well as theoretical, the book deserves to meet with a cordial reception both amongst those who would advance our knowledge in this fruitful and fascinating field, as well as at the hands of those who are engaged in the industrial applications of organic chemistry, to which latter class it cannot fail to prove of value.   A. G. P.

NOTE.

Note on Opium Analysis.

In my paper on opium analysis (this Journal **8**, 295), reference is made to the method of preparing the sample by kneading it on a slab of glass or wood. By the use of a small quantity of very fine dry starch, applied by means of a pepper-box with very small holes, this mixture is very much facilitated. The amount of starch needed is so small that it can make no difference in the percentage of morphia. Opiums containing 25 per cent. of water are easily manipulated with the use of starch, while without it they adhere badly to the hands and slab.

In comments which I have seen made upon my process of analysis this special point seems to have been overlooked—the presence of meconate of lime and other impurities in the crystallised morphia. These are not removed by the washing with the saturated solutions of morphia in alcohol and water, and the crystals therefore require the special treatment which I use in order to obtain the correct percentage of morphia present. If the extraction of the opium is done with the aid of lime, the meconate of lime is not present in the crystals, but the other impurities are to some extent, and the crystals still need purification before the final result is reached. But for reasons which I have given, the extraction with water alone is preferable to any other mode of treatment.   CHARLES M. STILLWELL.

AMERICAN

CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College.

LV.—THE ACTION OF FLUORIDE OF SILICON ON ORGANIC BASES.[1]

By Arthur M. Comey and C. Loring Jackson.

The research described in the following paper was undertaken in the hope of obtaining from the amines products similar to the compound which ammonia gives with fluoride of silicon, $(NH_3)_2SiF_4$, discovered by Gay-Lussac and Thenard,[2] and three years later prepared and studied by J. Davy.[3] We have been able to find only two previous papers on this subject, one published by Laurent and Delbos,[4] in 1848, in which the action of fluoride of silicon on aniline is described, the product being a nearly white mass, which they washed with ether, boiled with alcohol, and sublimed to purify it for analysis; their analyses, however, led only to a very complex formula containing oxygen, which they advance " with much reserve," although it was confirmed by the proportions[5] in which its factors combined. The substance when treated with water gave a gelatinous precipitate of silicic acid, and when boiled with alcohol was converted into small white

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[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] Mém. d'Arcueil **2**, 317.

[3] Phil. Trans. 1812, p. 352.

[4] Ann. chim. phys., ser. 3, **22**, 101.

[5] These proportions agree tolerably with the formula worked out by us for this substance, but their analytical results do not, and are entitled to no consideration, on account of the difficulties in the analysis, which Laurent and Delbos did not succeed in overcoming.

lustrous scales.[1] The second paper was published by W. Knop,[2] in 1858, and had for its primary object the study of the solution of fluoride of silicon in absolute alcohol, which gave with urea and aniline the fluosilicates of these bases, both of which Knop sublimed, and obtained from the urea fluosilicate only ammonic fluosilicate, silicic acid, and cyanuric acid; but from the aniline fluosilicate a new substance, which gave a precipitate of gelatinous silicic acid with water, and contained more silicon and fluorine than the fluosilicate. He did not, however, identify it with the substance made by Laurent and Delbos. We may add, that some years later W. Knop and W. Wolf[3] describe the aniline fluosilicate more in detail.

The results of our work on this subject may be summarised briefly as follows. Aniline forms with fluoride of silicon a compound having the formula $(C_6H_5NH_2)_3(SiF_4)_2$, which sublimes without alteration, but is decomposed with water, forming aniline fluosilicate and silicic acid; when heated with an excess of aniline it is converted into another compound having the formula $(C_6H_5NH_2)_4(SiF_4)_2$, and the same substance is formed when fluoride of silicon acts on aniline at high temperatures. This second product is unstable, breaking up spontaneously into the first and free aniline. The following bases also give compounds containing three molecules of the base to two of fluoride of silicon: paratoluidine, orthotoluidine, parachloraniline, diphenylamine, dimethylaniline, chinoline, and dimethylamine, the last giving also a compound having the formula $[(CH_3)_2NH]_4(SiF_4)_2$. On the other hand, we have not succeeded in obtaining from ammonia a compound of the formula $(NH_3)_3(SiF_4)_2$.

We propose to call these substances silicotetrafluorides, a clumsy name, it is true, but one which will designate them with certainty, whereas all the simpler names, such as silicofluoride or fluosilicide, have been used for the fluosilicates at one time or another, and might therefore lead to confusion.

The remainder of the paper contains the detailed account of our experimental results, and at the end a discussion of our views in regard to the constitution of the silicotetrafluorides.

PRODUCTS OF THE ACTION OF FLUORIDE OF SILICON ON ANILINE.

Trianiline disilicotetrafluoride, $(C_6H_5NH_2)_3(SiF_4)_2$.—This substance was prepared by passing fluoride of silicon over aniline.

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[1] Aniline fluosilicate.   [2] Chem. Centralblatt, 1858, p. 388.   [3] Ibid. 1862, p. 401.

The fluoride of silicon was made in the usual way, from calcic fluoride, sand, and sulphuric acid; but as we found that a glass flask after using it two or three times became perforated by the small quantities of hydrofluoric acid formed in the process, we replaced it by a thick glass bottle warmed in a water-bath, which lasted through a number of preparations. The delivery tube should not dip below the surface of the aniline, as in that case there is danger that it will be stopped by the product; but if it is brought near the surface of the base, the action takes place so rapidly that very little of the fluoride of silicon is lost. A good deal of heat is given out during the reaction, and the aniline is converted into a loose white solid, which was washed with hot ligroine until free from aniline, and then its purification finished by two sublimations. The yield was essentially quantitative, 30 grams of aniline giving after treatment with fluoride of silicon for 24 hours 51 grams of product, instead of 52 grams, the amount which should be obtained for the formula[1] $(C_6H_5NH_2)_3(SiF_4)_2$. The same substance is formed when aniline fluosilicate is sublimed, and the preparation, the analysis of which is numbered I, was made in this way. It is to be observed that the substance analysed by Laurent and Delbos was really prepared in this way, since by boiling their original product with alcohol they converted it into aniline fluosilicate, which was afterward reconverted into the silicotetrafluoride by sublimation. Also the substance obtained by Knop by sublimation of his aniline fluosilicate was the trianiline disilicotetrafluoride.

The method of analysis used for all these substances consisted in neutralising a weighed quantity of the substance dissolved in hot water in a platinum dish with a standard solution of sodic hydrate, using a solution of litmus as the indicator. The liquid was then heated to boiling, more of the sodic hydrate added, if the reaction had become acid, and evaporated to dryness on the water-bath, the residue treated with water, and the silicic dioxide filtered out. The filtrate, after neutralising once more with the sodic hydrate, which is usually necessary when the organic base is one with an alkaline reaction, $(NH_3$ or $(CH_3)_2NH)$, is treated with a solution of zincic oxide in ammonic carbonate, evaporated once more to dryness on the water-bath, treated with water, and filtered; the pre-

[1] Laurent and Delbos found that 59.5 grams of aniline absorbed 40.5 grams of fluoride of silicon. Our formula requires 44.3 grams.

cipitate is dissolved in strong nitric acid, evaporated to dryness, the residue after treatment with strong nitric acid extracted with water, and the silicic dioxide thus obtained added to that from the residue of the first evaporation, ignited, and weighed. The fluorine was usually calculated from the amount of the standard solution of sodic hydrate necessary for the neutralisation of the hydrofluoric acid present, but it was also occasionally determined direct in the filtrate from the zincic carbonate and silicate by evaporating to dryness in a platinum crucible, and, after removing any slight excess of sodic carbonate by converting it into acetate and washing with 80 per cent. alcohol, igniting and weighing as sodic fluoride.

I. 0.2686 gram of the substance gave 19.6 cc. of nitrogen at a temperature of 23° and a pressure of 768 mm.

II. 0.2982 gram of substance gave 0.0751 gram of silicic dioxide and 0.2105 gram of sodic fluoride.

III. 0.2842 gram of substance gave 0.0717 gram of silicic dioxide and 0.1968 gram of sodic fluoride.

IV. 0.3784 gram of substance needed for neutralisation 0.2480 gram of sodic hydrate.

	Calculated for $(C_6H_5NH_2)_3(SiF_4)_2$.	I.	II.	III.	IV.
			Found.		
Nitrogen	8.62	8.31			
Silicon	11.50	...	11.75	11.77	
Fluorine	31.24	...	31.94	31.33	31.15

Several attempts to make a combustion of the substance have shown that great difficulties stand in the way of getting satisfactory results, and, as the determinations of nitrogen, silicon, and fluorine just given are sufficient to establish its formula beyond a doubt, we have not thought it worth while to devote to the study of the conditions of its combustion the time necessary to obtain an accurate result.

Properties.—The trianiline disilicotetrafluoride is a white semi-crystalline to amorphous solid, which sublimes in the neighborhood of 200° without melting. It is insoluble in ether (anhydrous), benzol, ligroine, chloroform, or carbonic disulphide. It is decomposed very slowly by boiling absolute alcohol without any deposition of silicic acid, and converted into aniline fluosilicate ; we have not succeeded in bringing the other product of this reaction into a state fit for analysis ; it is a thick liquid, probably a silicic ethyl-ester. The action is more rapid with alcohol containing water.

Water decomposes it at once with deposition of silicic acid, and the solution yields on evaporation aniline fluosilicate[1] in beautiful white pearly scales. Its identity was determined by the following analysis:

0.7488 gram of substance gave by precipitation with baric chloride 0.6372 gram of baric fluosilicate.

	Calculated for $(C_6H_5NH_3)_2SiF_6$.	Found.
SiF_6	43.04	43.30

To determine the proportions in which the substances act on each other when water is added to the trianiline disilicotetrafluoride, we have studied the reaction quantitatively with the following results:

1.3092 grams of the substance were dissolved in water, and the silicic acid precipitated filtered out, ignited, and weighed, giving 0.1200 gram of silicic dioxide. To the filtrate was added potassic chloride, and the potassic fluosilicate formed was dried at 100° and weighed, giving 0.7370 gram.

These numbers agree best with the following reaction:

$$4(C_6H_5NH_2)_3(SiF_4)_2 + 6H_2O =$$
$$5(C_6H_5NH_3)_2SiF_6 + 2C_6H_5NH_3F + 3SiO_2,[2]$$
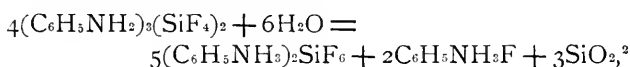
as is shown by comparing the amounts of the products which would be obtained from 100 grams of trianiline disilicotetrafluoride according to it, and those which were actually obtained in the experiment just described.

	Calculated from the Reaction.	Found.
Silicic dioxide	9.25	9.17
Aniline fluosilicate	84.70	84.41

Two attempts were made also to determine the amount of aniline fluoride formed (both by titration and by conversion into calcic fluoride); but although these experiments proved the presence of a fluoride, they gave results which did not agree with each other or with the theory, the reason being without doubt that a portion of the aniline fluoride was converted into fluosilicate during the filtrations, which we had to carry on in a glass funnel.

The action of ammonia gas upon the trianiline disilicotetrafluoride was studied carefully, since we hoped that it might throw light

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[1] W. Knop and W. Wolf, Chem. Centralblatt, 1862, p. 401.

[2] As a matter of fact, it was one of the silicic acids which was precipitated; but as we do not know which one it was, we prefer to write it as silicic dioxide.

on the constitution of this substance, and also that the correspond-
ing ammonia compound $(NH_3)_3(SiF_4)_2$ might be formed. Neither
of these hopes has been realised, however, for upon passing ammonia
gas over the trianiline disilicotetrafluoride the compound was
decomposed with a strong evolution of heat, aniline was set free,
and the product was the compound of ammonia and fluoride of
silicon already described by J. Davy, as was proved by the follow-
ing analyses, which also show that none of the desired substance
$(NH_3)_3(SiF_4)_2$ was formed ; and as it was not obtained under these
conditions, it is fair to suppose that it cannot exist. The substances
for Analyses I and II were prepared by washing the aniline out
of the crude product of the reaction with ligroine.   The substance
for Analysis III was further purified by sublimation.

I. 0.3414 gram of the substance gave 0.1496 gram of silicic dioxide
and 0.4154 gram of sodic fluoride.

II. 0.4400 gram gave 0.1937 gram of silicic dioxide.

III. 0.3770 gram gave 0.1625 gram of silicic dioxide.

IV. 0.1920 gram gave 0.0840 gram of silicic dioxide.

	Calculated for $(NH_3)_4(SiF_4)_2$.	I.	II.	III.	IV.
			Found.		
Silicon	20.29	20.44	20.55	20.12	20.41
Fluorine	55.07	55.03			

It was noticed during the purification of this substance that it
sublimed at a much higher temperature than the trianiline disilico-
tetrafluoride.   The reaction which takes place when trianiline
disilicotetrafluoride is treated with ammonia gas is the following :

$$(C_6H_5NH_2)_3(SiF_4)_2 + 4NH_3 = (NH_3)_4(SiF_4)_2 + 3C_6H_5NH_2,$$
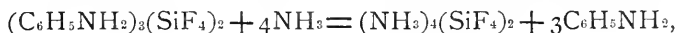
as was proved by its quantitative investigation.

2.8564 grams of trianiline disilicotetrafluoride yielded after treat-
ment with ammonia 1.6240 grams of $(NH_3)_4(SiF_4)_2$.

	Calculated Percentage according to the Reaction given above.	Found.
$(NH_3)_4(SiF_4)_2$	56.67	56.85

When hydrochloric acid gas is passed over trianiline disilico-
tetrafluoride there is no action in the cold ; but if the substance is
gently warmed, complete decomposition sets in, aniline chloride
sublimes along the tube in needles, and the hydrochloric acid con-
tains fluoride of silicon, as was shown by passing it into water,
when a precipitate of silicic acid was formed.

The action of ethyliodide was also tried. At 100° there was no action, but at 150° a product was formed which contained neither fluorine nor silicon, fluoride of silicon being given off when the tube was opened. Under these circumstances we did not think it worth while to try to purify the residual substance for analysis. Ethylbromide acted in the same way, but with more difficulty. Strong sulphuric acid decomposes trianiline disilicotetrafluoride, giving off fluoride of silicon. The action of the other common reagents with this substance could not be studied because it is decomposed by water or alcohol.

Dianiline silicotetrafluoride, $(C_6H_5NH_2)_4(SiF_4)_2$.—This substance was formed when aniline vapor was conducted into a receiver filled with fluoride of silicon, in the hope of preparing a compound containing a larger proportion of fluoride of silicon than that in the substance just described. The fact that, on the contrary, a body richer in aniline is formed, is probably to be accounted for by the high temperature at which the union of the two substances took place ; and this view is confirmed by some experiments in which we heated the trianiline disilicotetrafluoride with one molecule of aniline to 150° in a sealed tube for about five hours : the product was a purplish mass, which gave results on analysis showing that a considerable quantity of aniline had been taken up, although not quite enough to convert the trianiline disilicotetrafluoride completely into the dianiline silicotetrafluoride. As the substance prepared directly from aniline and fluoride of silicon could not be purified on account of its slight stability, it was analysed in the crude state with the following results, which are as accurate as could be expected under these circumstances :

I. 0.3803 gram of the substance gave 0.0826 gram of silicic dioxide and 0.2255 gram of sodic fluoride.

II. 0.3032 gram of the substance gave 0.0645 gram of silicic dioxide and 0.1798 gram of sodic fluoride.

	Calculated for $(C_6H_5NH_2)_4(SiF_4)_2$.	Found. I.	II.
Silicon	9.65	10.14	9 93
Fluorine	26.20	26.83	26.85

Properties.—It is a white powder which cannot be sublimed, as it decomposes with blackening when heated. With water it is decomposed and dissolved, with deposition of silicic acid. It is possessed of but slight stability, as it gradually decomposes

spontaneously even when kept in a corked tube at ordinary temperatures, the substance turning yellow and giving up aniline, which was extracted with ligroine, and recognised by its smell and its characteristic color with bleaching powder, while the residue was pure trianiline disilicotetrafluoride, as shown by the following analyses:

I. 0.2370 gram of the substance gave 0.0578 gram of silicic dioxide and 0.1637 gram of sodic fluoride.

II. 0.1236 gram of the substance gave 0.0841 gram of sodic fluoride.

	Calculated for		Found.	
	$(C_6H_5NH_2)_3(SiF_4)_2.$	$(C_6H_5NH_2)_4(SiF_4)_2.$	I.	II.
Silicon	11.50	9.65	11.39	
Fluorine	31.24	26.20	31.25	30.79

In view of this decomposition of the dianiline silicotetrafluoride into aniline and trianiline disilicotetrafluoride, and also of the formation of the dianiline silicotetrafluoride by heating aniline with trianiline disilicotetrafluoride, there seems no doubt that the real formula of this substance is $(C_6H_5NH_2)_4(SiF_4)_2$, that is, double the simplest formula determined by analysis, and that the reaction for its spontaneous decomposition is the following:

$$(C_6H_5NH_2)_4(SiF_4)_2 = C_6H_5NH_2 + (C_6H_5NH_2)_3(SiF_4)_2.$$

Action of Fluoride of Silicon on other Bases.

Triorthotoluidine disilicotetrafluoride, $(C_7H_7NH_2)_3(SiF_4)_2.$—
This substance was prepared by passing fluoride of silicon into a solution of orthotoluidine in benzol, when a very heavy gelatinous precipitate was formed, which was purified by washing with benzol and three sublimations. It can be formed also by the methods given under the aniline compound, but precipitation from a benzol solution gives the result more easily and furnishes a purer product. Its composition was determined by the following analyses:

I. 0.2100 gram of the substance gave 0.0476 gram of silicic dioxide.

II. 0.3530 gram of the substance gave 0.2177 gram of sodic fluoride.

III. 0.2330 gram of the substance gave 0.1440 gram of sodic fluoride.

IV. 0.2050 gram of the substance gave 0.1266 gram of sodic fluoride.

	Calculated for $(C_7H_7NH_2)_3(SiF_4)_2$.	I.	Found. II.	III.	IV.
Silicon	10.58	10.58			
Fluorine	28.73	...	27.90	27.97	27.94

Properties.—It is a white powder, subliming without melting or decomposition, like the corresponding aniline compound. It dissolves in hot common alcohol, and the solution deposits on cooling orthotoluidine fluosilicate in fine needles.

Triparatoluidine disilicotetrafluoride, $(C_7H_7NH_2)_3(SiF_4)_2$.—This substance was made and purified like the corresponding ortho compound, that is, by passing fluoride of silicon through a solution of paratoluidine in benzol, but even after four sublimations it had a distinct yellowish color. That the substance is essentially pure, however, in spite of this coloration, is shown by the following analyses :

I. 0.1928 gram of the substance gave 0.0438 gram of silicic dioxide.

II. 0.1472 gram of the substance gave 0.0922 gram of sodic fluoride.

	Calculated for $(C_7H_7NH_2)_3(SiF_4)_2$.	Found. I.	II.
Silicon	10.58	10.60	
Fluorine	28.73	...	28.34

In properties it resembles the corresponding ortho compound, but is decidedly less stable, showing a strong tendency to turn yellow on standing ; and the paratoluidine fluosilicate deposited as the hot solution of the substance in alcohol cools, crystallises in thick needles.

Trimonochloraniline disilicotetrafluoride, $(C_6H_4ClNH_2)_3(SiF_4)_2$. This substance was made by passing fluoride of silicon over parachloraniline, and was purified by sublimation. Its composition was determined by the following analysis :

0.4807 gram of the substance gave 0.0990 gram of silicic dioxide and 0.2686 gram of sodic fluoride.

	Calculated for $(C_6H_4ClNH_2)_3(SiF_4)_2$.	Found.
Silicon	9.48	9.61
Fluorine	25.75	25.29

It resembles the corresponding aniline compound in its properties, and forms with hot alcohol a solution of the parachloraniline fluosilicate, which separates as the solution cools in beautiful long slender needles.

Parabromaniline forms a similar compound with fluoride of silicon, and gives with hot alcohol a solution depositing the parabromaniline fluosilicate in small pearly scales.

With *symmetrical tribromaniline* we could get no action, when we treated it with fluoride of silicon, the result of the experiment being negative, whether it was acted on alone in the solid state, or fused, or in solution in benzol. Symmetrical tribromaniline therefore does not combine with fluoride of silicon under the conditions which bring about the union with it of all the other bases studied.

Tridiphenylamine disilicotetrafluoride, $[(C_6H_5)_2NH]_3(SiF_4)_2$.— Solid pure diphenylamine is not acted on by fluoride of silicon ; the statement made in a preliminary notice of this work, that a compound was formed under these conditions, was incorrect, the diphenylamine used for that first experiment being impure. If, however, fluoride of silicon is passed through a solution of diphenylamine in benzol, a white crystalline precipitate is deposited slowly, which was washed with benzol, dried at 100°, and analysed with the following results :

I. 0.4356 gram of the substance gave 0.0695 gram of silicic dioxide and 0.2141 gram of sodic fluoride.

II. 0.4192 gram of the substance gave 0.1986 gram of sodic fluoride.

	Calculated for $[(C_6H_5)_2NH]_3(SiF_4)_2$.	Found. I.	II.
Silicon	7.83	7.44	
Fluorine	21.26	22.23	21.43

Properties.—It forms thick white needles, which are decomposed by heat into fluoride of silicon and diphenylamine. When treated with water a precipitate of diphenylamine separates, and the filtrate contains fluosilicic acid. A quantitative study of the reaction gave the following results :

I. 0.8135 gram of the substance gave 0.5686 gram of diphenylamine and 0.3040 gram of potassic fluosilicate.

II. 0.4934 gram of the substance gave 0.3476 gram of diphenylamine.

In the calculated percentages given below it is assumed that all the diphenylamine is separated by the action of the water, and that four molecules of the compound will yield five of potassic fluosilicate, *i. e.* that the reaction with water is analogous to that of the corresponding aniline compound.

	Calculated.	I.	Found. II.
Diphenylamine	70.91	69.89	70.44
Potassic fluosilicate	38.50	37.37	

If, as the numbers obtained seem to show, the reaction is similar to that of the trianiline disilicotetrafluoride with water, silicic acid should have been set free, but no trace of it could be discovered, the solution being free from any precipitate except the diphenylamine, and upon evaporation to dryness leaving no residue, while that silicic acid had not been carried down by the diphenylamine was shown by burning it and also by dissolving it in benzol. In neither case did it leave a residue. We have not been able to find any explanation for this curious observation, or to account for the formation of fluosilicic acid without the formation of silicic acid at the same time. That the soluble product was principally fluosilicic acid is proved by the fact that it gave a precipitate with potassic chloride.

Tridimethylaniline disilicotetrafluoride, $[C_6H_5N(CH_3)_2]_3(SiF_4)_2$. —Fluoride of silicon has no action on dimethylaniline alone, but, if the gas is passed through a solution of dimethylaniline in benzol, a flocculent precipitate is formed, which is gradually converted into a gummy mass that crystallises on standing. The crystals were purified by washing with benzol and ligroine, dried at 100°, and analysed.

0.1066 gram of the substance gave 0.0220 gram of silicic dioxide and 0.0584 gram of sodic fluoride.

	Calculated for $[C_6H_5N(CH_3)_2]_3(SiF_4)_2$.	Found.
Silicon	9.81	9.63
Fluorine	26.62	24.77

The number for the fluorine is far from satisfactory, which is accounted for by the difficulty of purifying this decidedly unmanageable substance. It is, however, near enough to show that the substance can have no other composition than that assigned to it by us.

Properties.—It forms an indistinct crystalline mass, which is decomposed by heat, and gives no stable fluosilicate, when treated with alcohol.

Trichinoline disilicotetrafluoride, $(C_9H_7N)_3(SiF_4)_2$.—Chinoline alone is not acted on by fluoride of silicon; but, if the gas is passed

through a solution of chinoline in benzol, a gummy precipitate is formed at first, which becomes gradually converted into needle-shaped crystals. The product was purified by washing with benzol or ligroine, and dried at 100°. The same substance is obtained when chinoline fluosilicate is sublimed, and the analysis numbered II is of a preparation made in this way.

I. 0.1634 gram of the substance gave 0.0323 gram of silicic dioxide.

II. 0.0730 gram of the substance gave 0.0404 gram of sodic fluoride.

	Calculated for $(C_9H_7N)_3(SiF_4)_2$.	Found. I.	II.
Silicon	9.41	9.23	
Fluorine	25.55	...	25.01

Properties.—It crystallises in needles, and sublimes without melting or decomposition. Although hot alcohol usually decomposes it, as described below, on one occasion it dissolved it without decomposition, and this solution gave on cooling thick needles, which gave the following results on analysis :

0.0903 gram of the substance gave 0.0176 gram of silicic dioxide and 0.0506 gram of sodic fluoride.

	Calculated for $(C_9H_7N)_3(SiF_4)_2$.	Found.
Silicon	9.41	9.10
Fluorine	25.55	25.38

On addition of water the substance analysed was decomposed with deposition of silicic acid. We have not succeeded, however, in repeating this experiment, as in all other cases the product from the action of hot alcohol has been chinoline fluosilicate, which crystallises in long thick needles as the solution cools, and gives a clear solution with water. Its composition was determined by the following analyses of the substance purified by two crystallisations :

I. 0.1244 gram of the substance gave 0.0200 gram of silicic dioxide.

II. 0.2054 gram of the substance gave 0.0325 gram of silicic dioxide and 0.1254 gram of sodic fluoride.

	Calculated for $(C_9H_7N)_2H_2SiF_6$.	Found. I.	II.
Silicon	6.96	7.50	7.38
Fluorine	28.35	...	27.64

The trichinoline disilicotetrafluoride resembles the corresponding aniline compound closely in its properties.

Didimethylamine silicotetrafluoride, $[(CH_3)_2NH]_4(SiF_4)_2$.— When dry dimethylamine (prepared according to Baeyer and Caro) was mixed with fluoride of silicon, a white powder was deposited, which was analysed in the crude state, since it could not be purified because of its very slight stability.

0.2320 gram of the substance gave 0.0740 gram of silicic dioxide and 0.2038 gram of sodic fluoride.

	Calculated for $[(CH_3)_2NH]_4(SiF_4)_2$.	Found.
Silicon	14.43	14.89
Fluorine	39.17	39.75

Properties.—A white solid, which, like the corresponding compound of aniline, is very unstable, decomposing spontaneously at ordinary temperatures into dimethylamine and the following compound—a decomposition which is hastened by heat.

Tridimethylamine disilicotetrafluoride, $[(CH_3)_2NH]_3(SiF_4)_2$.— This substance was made by subliming the compound just described, when dimethylamine was given off as a secondary product. It was purified by a second sublimation, and its composition determined by the following analyses:

I. 0.1871 gram of the substance gave 0.0660 gram of silicic dioxide.

II. 0.2800 gram of the substance gave 0.0960 gram of silicic dioxide and 0.2694 gram of sodic fluoride.

	Calculated for $[(CH_3)_2NH]_3(SiF_4)_2$.	Found. I.	Found. II.
Silicon	16.33	16.46	16.00
Fluorine	44.31	...	43.53

Properties.—It is a white powder, resembling the corresponding aniline compound in appearance and behavior when heated, although it sublimes at a higher temperature. It also differs from the aniline compound in being deliquescent.

Finally, we may add the following experiments, which gave products of so little promise that we did not attempt to analyse them, but which show that fluoride of silicon acts also on alkaloids, and on amides which can form salts.

Furfurine, when treated in benzol solution with fluoride of silicon, gave a gummy mass similar to that obtained from dimethylaniline, which, however, did not crystallise on standing.

Dry powdered *urea* was converted by fluoride of silicon into a pasty mass, which was decomposed with evolution of ammonia when the attempt was made to sublime it. The sublimate contained fluorine and silicon, but we did not continue the study of it, as we had no guaranty that it was a homogeneous substance.

CONSTITUTION OF THE SILICOTETRAFLUORIDES.

Although we have not succeeded in obtaining an absolute direct proof of the constitution of the substances described in this paper, we have been able to reduce the possible formulas that can be assigned to them to a very small number by the following course of reasoning. In the first place, we assume that all the substances described in this paper, which contain three molecules of the base combined with two of fluoride of silicon, have the same constitution; an assumption which is justified by the fact that they are all made by the direct addition of fluoride of silicon to the base, and also by the strong resemblance in their properties, the differences observed being such as might well occur among substances belonging to the same class.

Upon considering, in general, the way in which the fluoride of silicon could attach itself to a base, we have been able to find only three probable methods, which we will proceed to discuss as applied to our compounds. (*a.*) By replacing the hydrogen of the amido group, forming a substance which would be at once an anilid and a fluosilicate. This method would seem at first sight the most probable, especially since A. Harden[1] has found that chloride of silicon gives with aniline $SiCl_2(NHC_6H_5)_2$ and aniline chloride; but this mode of union is impossible, since both chinoline and dimethylaniline, which contain no hydrogen attached to their nitrogen, form compounds of this class. (*b.*) By the action of the fluoride of silicon on the benzol ring, forming a substance analogous to pararosaniline fluosilicate. This hypothesis, which is improbable on account of the ease with which the substances are broken up by water, is rendered entirely inadmissible by the formation of the dimethylamine compound, which contains no ring. (*c.*) On the supposition that the fluoride of silicon combines with the base to form a sort of salt, this view is the only one compatible with our results, and its correctness is confirmed by the observation that all the substances tried formed salts, with one

[1] J. Lond. Chem. Soc. 1887, **1**, 40.

exception, tribromaniline, and that this was the only one which did not form a silicotetrafluoride; further, the stability of the silicotetrafluorides keeps pace with the stability of the salts of the bases; those like aniline, the two toluidines, parachloraniline, chinoline, and dimethylamine, which form stable salts, giving silicotetrafluorides which can be sublimed without decomposition, whereas diphenylamine and dimethylaniline gave compounds decomposed by heat. That the salts of diphenylamine are unstable, being decomposed by water, is well known, and although we have not been able to find any published statement about the salts of dimethylaniline that would imply they are unstable, our own work has furnished the proof that the fluosilicate at least is less stable than that of aniline, as only the products of the decomposition of the fluosilicate were obtained when water was added to the tridimethylaniline disilicotetrafluoride.

We infer, then, from the arguments given above, that the nitrogen in the silicotetrafluorides is in the quinquivalent condition, and think it most probable that one of the two additional bonds is satisfied by silicon, the other by fluorine, and that the following graphic formula represents its constitution. It should be remembered, however, that this formula is only the most probable one, for, as already stated, we have been able to bring no absolute proof of its correctness.

$$C_6H_5 \overset{H_2}{=} N - F_2 - Si \overset{H_2 = N - C_6H_5}{=\!=\!=\!=} F_2 \overset{}{=\!=\!=\!=} Si - F_2 - N \overset{H_2}{=} C_6H_5.$$

If this formula is adopted, the formation of the silicotetrafluorides can be explained in the following way. In the first place one molecule of the fluoride of silicon acts upon one molecule of the base to give the group

$$C_6H_5 \overset{H_2}{=} N \overset{- SiF_3,}{-F}$$

and, although this mode of union seems strange at first sight, it is not without analogy, if we consider the close relationship of silicon and carbon, as then it is similar to the formation of ammonium salts by the action of methyliodide on a base, as shown by the following reactions:

$$C_6H_5NH_2 + CH_3I = C_6H_5 \overset{H_2}{=} N \overset{- CH_3}{-I};$$
$$C_6H_5NH_2 + SiF_3F = C_6H_5 \overset{H_2}{=} N \overset{- SiF_3.}{-F}$$

Since the group

$$\underset{C_6H_5-}{\overset{H_2=}{}}N\underset{-F}{\overset{-SiF_3}{}}$$
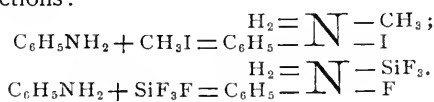
is at once a fluoride and a substituted fluoride of silicon, an action
next takes place similar to the formation of a fluosilicate from a
fluoride and fluoride of silicon, thus :

$$\underset{C_6H_5-}{\overset{H_2=}{}}N\underset{-F}{\overset{-SiF_3}{}}=\underset{C_6H_5-}{\overset{H_2=}{}}N\underset{-F=F-}{\overline{}}Si=F_2 ;$$

$$_2KF + SiF_4 = \underset{K-F=F-}{\overset{K-F=F-}{}}Si=F_2.$$
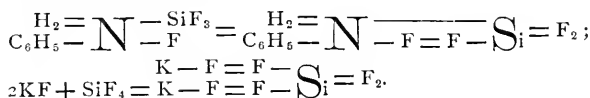
In this reaction the formation is assumed of the bivalent radical
F_2^{II}, which has been proved to exist in hydrofluoric acid by
Mallet's determination[1] of the vapor density leading to the formula
H_2F_2, and the assumption of the presence of which in fluosilicic
acid explains its relation to silicic acid in the most satisfactory way.
The substance

$$\underset{C_6H_5-}{\overset{H_2=}{}}N\overline{-F_2-}Si=F_2$$
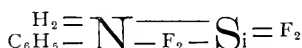
next acts on another molecule of the base in the same way that the
fluoride of silicon did originally, forming

$$\underset{C_6H_5-}{\overset{H_2=}{}}N\overline{-F_2-}Si\underset{-F}{\overset{H_2=}{=}}N\underset{-F}{\overset{-C_6H_5}{}} ;$$
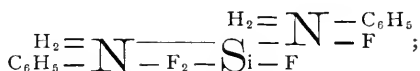
but it would seem that the acid nature of the silicon has been so
weakened by the introduction of two aniline molecules, that the
atom of fluorine left attached to the silicon cannot combine with
the fluorine attached to the nitrogen, and therefore this latter is
saturated by the more acid fluorine of a fluoride of silicon carrying
only one aniline molecule, thus :

$$\underset{C_6H_5-}{\overset{H_2=}{}}N\overline{-F_2-}Si\underset{-F}{\overset{H_2=N-C_6H_5}{=}}{\overset{-F}{}} + \underset{F-}{\overset{F-}{}}Si\overline{-F_2-}N\underset{-C_6H_5}{\overset{=H_2}{}}$$

$$= \underset{C_6H_5-}{\overset{H_2=}{}}N\overline{-F_2-}Si\underset{-F}{\overset{H_2=N-C_6H_5}{=}}\underset{F-}{\overset{-F_2-}{}}Si\overline{-F_2-}N\underset{-C_6H_5}{\overset{=H_2}{}} .$$
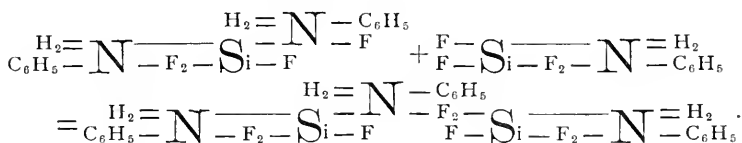
If, then, the two atoms of fluorine remaining attached simply to
silicon are united, the formula given above is constructed.   Our
only reason for joining these last atoms of fluorine is that it makes
the molecule more symmetrical, but it is also possible that they
remain univalent.

Turning next to the compounds formed by the union of the base

[1] This Journal **3**, 189.

and fluoride of silicon in the proportion of two molecules of the former to one of the latter; as has been already argued, it is necessary to double the simplest formula which can be assigned to these substances, because they break up into the free base and the compound of three molecules of the base to two of fluoride of silicon, and also because they can be formed by a reaction the reverse of this decomposition. If, then, the formula discussed above is given to the trianiline disilicotetrafluoride, the formula of the dianiline silicotetrafluoride must be

$$\underset{C_6H_5-}{\overset{H_2=}{N}} - F_2 - \underset{H_2=}{Si} - \overset{H_2=N-C_6H_5}{\underset{-C_6H_5}{N}} - Si - F_2 - \underset{-C_6H_5'}{\overset{=H_2}{N}}$$
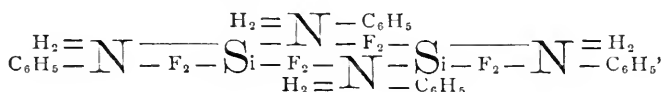
and the very slight stability of the substance can be explained by the neutralisation of the acid properties of the silicon and fluorine, already alluded to, by the introduction of so many molecules of base, which makes them hold the last molecule of the base with comparatively little force. On the other hand, we have not been able to find any explanation for the stability of the compound derived from ammonia, as the only one we could think of—viz. that the ammonia being a stronger base than aniline would attach itself more firmly to the slightly acid molecule—is rendered inadmissible by the slight stability of the compound made from dimethylamine, a base nearly, if not quite, as strong as ammonia itself. It is possible that the ammonia compound has an entirely different constitution from the compounds of the organic bases, but we have no experimental material for testing the correctness of this hypothesis except Mixter's determination[1] of the vapor density of this substance, which showed that it was dissociated into four volumes of ammonia and two of fluoride of silicon, and therefore that the simplest formula of the ammonia compound must be doubled, which would look as if it had a constitution similar to the organic compounds.

We may add that Harden[2] obtained by the action of chloride of silicon on pyridine, or chinoline compounds $(C_5H_5N)_2SiCl_4$, and $(C_9H_7N)_2SiCl_4$; but as they give up chloride of silicon spontaneously, it is probable that they are not analogous in constitution to our substances.

The study of the action of fluoride of silicon on organic bases will be continued by one of us in this laboratory.

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[1] This Journal **2**, 153.   [2] J. Lond. Chem. Soc. 1887, **1**, 40.

13

LVI.—A DETERMINATION OF THE RELATION OF THE ATOMIC WEIGHTS OF COPPER AND SILVER.

By Theodore W. Richards.

In the Report of the Committee on Electrolysis made to the British Association at Birmingham, of which an advance copy has been received by Professor Cooke through the kindness of Dr. Oliver Lodge, a direct determination is given of the ratio between the atomic weight of copper and that of silver, based on the electrolytic experiments of W. N. Shaw. As the value of the ratio thus obtained is quite different from that usually accepted, it seemed to Professor Cooke desirable that the results should be confirmed by a direct chemical method, and the writer was intrusted with this investigation.

Of the work worthy of consideration which has thus far been done upon the atomic weight of copper, first in chronological order comes that of Berzelius,[1] who made two determinations of the weight of copper formed by the reduction of pure cupric oxide by hydrogen. He found the percentage of copper in this compound to be $79.823 \pm .002$. This corresponds to an atomic weight of 63.153, taking oxygen $= 15.963$, with Clarke. The next determination was by Erdmann and Marchand,[2] who used the same method. They found the percentage of copper in cupric oxide to be 79.8645 $\pm .0038$ as a mean of four determinations—a value which makes $Cu = 63.316$. Millon and Commaille,[3] in three determinations—which did not, however, closely agree with one another—found the relation $CuO : Cu = 100 : 79.7787$; and calculating from this relation the atomic weight of copper, the value 62.979 is obtained. Dumas[4] made several determinations of the reduction of cupric oxide and the synthesis of cuprous sulphide, and calculates the value $Cu = 63.5$.

Hampe,[5] whose work gave the most concordant results thus far secured, obtained from three determinations of the percentage of copper in cupric oxide the mean value of $79.8347 \pm .0013$; and from two analyses of anhydrous cupric sulphate by electrolytic precipitation he found the proportion $CuSO_4 : Cu = 100 : 39.725$ $\pm .0007$. The atomic weights of copper from these two methods are respectively 63.197 and 63.173.

[1] Poggend. Annal. **8**, 177.   [2] J. prakt. Chem. **31**, 389 (1844).
[3] Ztschr. anal. Chem. **2**, 475 (1863).   [4] Ann. chim. phys. (3) **55**, 129.
                    [5] Ztschr. anal. Chem. **13**, 352 (1874).

This was in 1874; and the subject has rested undisturbed until last year, when W. N. Shaw, in the paper before referred to, sought to prove the accuracy of Faraday's law of electrolysis in atomic proportions, by means of the actual weights of silver and copper deposited in cells in the same circuit. For the particulars of his method the Report of the Committee on Electrolysis should be consulted; it is sufficient here to say that as the mean of many determinations he finds the ratio of the silver and copper precipitated to be 3.39983 : 1. Correcting this result for variations in current density, he obtains the value 3.39888, and finally adopts the practically identical value 3.400, which makes the ratio Ag : Cu = 17 : 10. This last value makes Cu = 63.333, while the corrected value gives as the atomic weight the quantity 63.360.

Below is a summary of all the results :

Berzelius, from CuO 63.153
Erdmann and Marchand, from CuO 63.316
Millon and Commaille, from CuO 62.979
Dumas, from CuO and Cu₂S 63.5
Hampe, from CuO 63.197
    "   from CuSO₄ 63.173
W. N. Shaw, by relation to silver 63.333
    "   "   "   corrected 63.360

The most obvious chemical method for the determination of the relation of the atomic weights of silver and copper is by the precipitation of silver from a solution of a pure silver salt by means of pure copper; and this was the method adopted in the present determination. Hampe, in his work on the atomic weight of copper, attempted the same method, but rejected it for two reasons—the first being that the silver dissolved, or appeared to dissolve, to a slight extent in the hot water used for washing; and the second being that it was impossible to prevent copper from coming down with the silver, no matter how long the precipitate was digested with the argentic nitrate solution. As will be seen, however, both of these difficulties have been entirely overcome.

The silver salt selected for the precipitation was the nitrate, on account of its ready crystallisation, its easy solubility in water, and the facility with which it can be obtained pure. For the preparation of the salt used in the work, ordinary pure argentic nitrate was crystallised many times from hot water, and finally fused for

two hours in an air-bath kept at 205° C.—a few degrees above its melting point.   This preparation was a white translucent substance interspersed with transparent crystals, dissolving completely in water, and giving a colorless solution which was wholly neutral.

The copper used was prepared by electrolysis from cupric sulphate, through the kindness of Mr. Wilson, of the University Press. It was cut into small pieces, and these were digested in succession with weak potassic hydrate, dilute sulphuric acid, and then a very large amount of water.   The copper was then boiled with water for about half an hour and washed with a large amount of distilled water, then dried and reduced at a low red heat by means of perfectly pure hydrogen, and allowed to cool in a stream of the gas. The metal thus prepared had a beautiful red metallic lustre, and showed no trace of oxidation after keeping a month.   Before use it was dried in an air-bath at 110°, allowed to cool in a desiccator, and weighed by itself on a balance which was distinctly sensible to a twentieth of a milligram.   In addition to receiving the treatment described above, the copper used in the fifth and sixth experiments was oxidised in a stream of pure air for half an hour, and then again reduced by hydrogen ; but the concordance of those two results with the others shows that this precaution was not necessary.

In a few preliminary experiments it was found that on the temperature of the solution, and on the temperature alone, depended the regularity with which the silver was precipitated by the copper. At 90° the deposition is very rapid, nitrous fumes are evolved, and a large amount of copper comes down with the silver.   As the temperature of the solutions used is lower, the reaction becomes less rapid, and the amount of copper deposited with the silver less, until at ordinary temperatures it is comparatively small ; and below 0° the silver comes down absolutely pure, and not the least evolution of gas is observed.   One of the difficulties of Hampe can then be overcome by keeping the beaker containing the solution in a freezing mixture ; and the perfect definiteness of the reaction, which before might have been questioned, is thus established. The duration of the reaction at —1° is from twelve to twenty-four hours, according to the dilution of the argentic nitrate.   The more dilute the solution is, the longer the precipitation takes, and the more finely divided is the deposited silver; but when the solution is very concentrated, the reaction is completed in a comparatively short time, and the silver comes down in a beautiful compact crystalline crust which takes the form of the copper.

The silver which was formed was collected in a Gooch crucible and washed with cold water, of which less than 250 cc. were necessary to give a filtrate in which no trace of silver or copper could be detected.

The fact that the determinations given below agree so exactly with each other is of itself proof that no silver was dissolved—first, because the precipitate in the different experiments was of very different degrees of fineness ; and secondly, because the precipitate in each experiment was washed with a different amount of water, the silver of the last experiment having at least four times as much water passed over it as that of the first. And the fact that the results are not affected by either circumstance shows clearly that no perceptible amount of silver could have been dissolved ; for if so, the loss must have varied both with the condition of the precipitate and with the amount of the wash water. The different result obtained by Hampe was probably the effect of hot water on a very finely divided precipitate.

The silver, whether in crystalline plates or in crystalline powder, formed a very convenient precipitate with which to work ; it was easily transferred and easily washed, did not adhere to the glass, and was in every way adapted for quantitative work.

The conditions of the following experiments as regards the quantity of water and the excess of argentic nitrate used above the amount required to dissolve the copper, were varied as much as possible. In some determinations barely enough of the argentic nitrate was used to effect the solution, while in others the excess of the silver salt amounted to nearly two grams. The time allowed the reactions was also varied from twenty-four to seventy-two hours.

Relation of Silver to Copper.

No. of Expt.	cc. H_2O used.	Weight Cu taken.	Weight Ag formed.	Equivalent $Ag_2 : Cu = 1 : n$.	Atomic Weight Cu $Ag = 108$.	$Ag = 107.675$.
I	20	0.53875	1.8292	0.29452	63.618	63.427
2	25	0.56190	1.9076	0.29456	63.624	63.432
3	120	1.00220	3.4016	0.29462	63.639	63.447
4	30	1.30135	4.4173	0.29462	63.638	63.447
5	20	0.99870	3.39035	0.29457	63.628	63.437
6	25	1.02050	3.4646	0.29456	63.623	63.434
			Average,	0.29457	63.628	63.437

The mean value, 63.437, has a greatest variation of $\pm$.01 and a probable error of $\pm$.0023.

The value obtained by Shaw was 63.333
"   "   "   "   corrected . . . 63.360
The value given by Clarke is 63.173

It remains only to prove the absolute purity of the copper used and the silver formed. The only metals which could affect the atomic weight of copper to an appreciable extent, if present in traces, are bismuth and silver. The former was tested for with great care, using a delicate spectroscope, and not the faintest trace of the very well-defined blue bismuth line was apparent; further, ten grams of the copper were dissolved in nitric acid, a little potassic hydrate added to the diluted solution, and the whole boiled and shaken for three hours. According to Hampe, all the bismuth present will be found in the basic precipitate; this was tested qualitatively for the metal, and not a trace was found. The solution of a portion of the copper in pure nitric acid gave not the faintest trace of opalescence with hydrobromic acid, excess of ammonic hydrate, or baric chloride. A gram of the copper was tested for arsenic and antimony in a Marsh-Berzelius apparatus, and no trace of a mirror was obtained. As the presence of so much copper would cause the generator to run too rapidly, the solution was treated with just enough potassic ferrocyanide to effect precipitation, and the colorless filtrate was run into the apparatus. This method has been found to give good results. The copper and the precipitated silver each dissolves in nitric acid without leaving a trace of residue.

If the copper is pure, the only possible impurity which the silver could contain is copper; and this was tested for with great care in each precipitate by dissolving one to two grams in nitric acid and adding excess of ammonic hydrate. In no case was the slightest blue color noticed; and as under the same circumstances a tenth of a milligram of copper gave a distinct bluish tinge, it may be assumed that the silver contained no copper. This method is a convenient one for the preparation of chemically pure silver, and avoids the necessity of fusion and the concomitant absorption of oxygen and possible admixture of silicic anhydride.

Although the value of the atomic weight of copper obtained, 63.44, does not exactly coincide with Shaw's results, it is at least

very much nearer to them than is the old accepted value of 63.17; especially if we take his result as corrected for current density. The new value is very nearly that found by Dumas from cuprous sulphide, and it falls within the limits assigned by L. Meyer and Seubert as the possible error of the accepted value.

LVII.—FURTHER INVESTIGATION ON THE ATOMIC WEIGHT OF COPPER.

By Theodore William Richards.

After the investigation described in the preceding article was completed, it became necessary, in the course of some further experiments, to ignite a portion of the silver from determination No. 5 of that series, and it was found that two grams of silver lost four tenths of a milligram by this process. It is thus evident that 150° is not a temperature high enough to drive out all the water from the silver, and hence the results before given are incorrect by a slight amount. In this determination the weight of the silver was 3.39035 grams after drying at 150°, hence its weight after ignition would have been 3.38975 grams. The weight of copper taken was .9987 gram, therefore the corrected atomic weight of copper would be 63.452 instead of 63.437.

Unfortunately, all the silver formed in the other determinations had been employed in testing for the presence of copper; hence it was impossible to determine whether the other samples would lose water on heating in a similar manner. It seemed, therefore, desirable to make a new series, using samples of pure copper prepared from the ores of different localities. Should the result be the same in each instance we should have a very strong proof, not only that the copper used in each case was pure—because the different samples would probably contain different impurities—but also that the atomic weight of copper is a perfectly constant quantity.

The method used was exactly that of the previous paper, although more difficulty was found in keeping the solution below zero for twenty-four hours than was the case before, because of the warmer weather. Several determinations had to be rejected because the temperature rose above zero and copper was precipitated with the silver. Upon splitting open the fine crystalline plates of silver precipitated in these rejected experiments, a light

green precipitate of basic cupric nitrate was found adhering to the inner surface, which could not be removed by continued washing with cold water. The presence of this precipitate explains the admixture of copper with the silver precipitated above zero, and points at once to the mechanism of the chemical action.

When copper is placed in a solution of argentic nitrate, two reactions take place, and the temperature regulates the predominance of one or the other. The chief reaction is the simple one ordinarily written; it alone is active between $0°$ and $-5°$, and it is the chief one even at $100°$. The secondary reaction, which is active at $100°$, but which entirely ceases below $0°$, may perhaps be written thus—assuming that the basic nitrate has the formula usually assigned to it:

$$4AgNO_3 + 4Cu + 3H_2O =$$
$$Cu(NO_3)_2 . 3Cu(OH)_2 + 2Ag_2 + NO + NO_2.$$
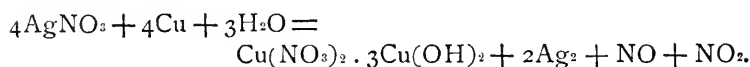
Evidently in this reaction the copper precipitates only one half of its equivalent of silver. It will be remembered that an evolution of nitrous fumes was previously observed when the temperature rose above the freezing point.

The argentic nitrate used in the new series was prepared as before, except that even greater precautions were taken to insure its purity, by successive crystallisations and fusions.

Two samples of copper were used, one from Lake Superior, the other from Germany. For the purification of the former the sample was dissolved in sulphuric acid, with the addition of nitric acid; the solution was evaporated to dryness, and the solid heated over asbestos in a porcelain dish, until the fumes of sulphuric acid ceased coming off. The cupric sulphate was now dissolved in water, crystallised twice, and the diluted solution of the last crystals boiled and shaken with a little potassic hydrate for three hours. The solution was now filtered, and the cupric sulphate was crystallised several times from hot water. Finally, the solution of the last pure crystals, strongly acidified by sulphuric and a little nitric acid, was decomposed by the current of a Bunsen cell, and the chemically pure copper deposited on thick platinum foil.

The second sample of copper was prepared from German cupric oxide in a similar manner, except that the sulphate was crystallised a greater number of times. In this connection it may be mentioned that, of many samples of German cupric oxide tested, not one was found that did not contain a comparatively large amount of arsenic.

In the case of many samples, after several reductions with pure hydrogen and oxidations, the arsenic will actually sublime off as arsenious oxide; and a quantity of the substance was collected in this manner.

The method of cleaning the copper was similar to that previously adopted; it was treated in succession with dilute potassic hydrate, dilute sulphuric acid, and a very large amount of water, and then dried and reduced by pure hydrogen.

The silver which was obtained by precipitation from the pure argentic nitrate was first washed and dried at 150°, and weighed, as before; and was then heated to incipient redness, and weighed again. The loss of weight by this process varied with the different samples between three tenths of a milligram and one milligram. The Gooch crucible and asbestos mat subjected to the same treatment did not lose an appreciable quantity. The results were calculated for the weight of silver both before and after ignition, and it will be noticed that the first column of results corresponds almost exactly to the results given in the previous paper. The silver was in each case tested for copper, and no trace was found.

RESULTS.

German Copper.

No. of Experiment.	Weight Cu.	Weight of Silver formed.		$Cu : Ag_2 = 1 : n.$	Atomic Weight Cu $(Ag = 107.675)$.	
		Before Ignition.	After Ignition.		Before Ignition.	After Ignition.
	Grams.	Grams.	Grams.			
1	0.75760	2.5723	2.5713	3.3940	63.426	63.450
2	0.95040	3.2261	3.2256	3.3939	63.440	63.451
3	0.75993	2.5798	2.5794	3.3942	63.438	63.447

Average, 63.449

Greatest variation $= \pm .002$.   Probable error $= \pm .0010$.

Lake Superior Copper.

No. of Experiment.	Weight Cu.	Weight Ag formed.		$Cu : Ag_2 = 1 : n.$	Atomic Weight Cu $(Ag = 107.675)$.	
		Before Ignition.	After Ignition.		Before Ignition.	After Ignition.
	Grams.	Grams.	Grams.			
4	1.02060	3.4650	3.4640	3.3942	63.432	63.448
5	0.90460	3.0705	3.0701	3.3939	63.444	63.452

Average, 63.450

Greatest variation $= \pm .002$.   Probable error $= \pm .0013$.

The average of these two series is 63.450, with greatest varia-
tions of $+$.002 and $-$.003, and a probable error of $\pm$.0006. The
average of the results calculated from the weight of silver dried at
150° is 63.436, while the results published in the preceding paper
gave 63.437.

The complete concordance of these results with each other and
with the previous value above referred to, would point strongly to
the following conclusions.

First, that the copper used in each case was absolutely free
from metallic alloy; for manifestly the three entirely different
samples would be likely to contain different impurities, or at least
different amounts of the same impurity. The copper was tested
for sulphur with the greatest care by solution in nitric acid and
treatment with baric chloride, and no trace of cloudiness was per-
ceptible. That the copper was *absolutely* free from impurity is
not contended; only that it did not contain a weighable amount of
impurity in one gram, the amount used in each experiment. It
is manifest that attempts to purify the copper beyond this limit
would be labor thrown away and would produce no effect upon
the atomic weight. For example, one tenth of a milligram is a
very large amount of foreign material to suppose existing in a gram
of copper purified with such care; but this large amount would
only change the atomic weight five units in the third decimal place,
a quantity which is of no consequence when the atomic weight is
in doubt three units in the first decimal place.

Another and still more positive conclusion reached by these
results is that the atomic weight of copper is a constant quantity
with reference to nitric acid and silver. If copper had a variable
atomic weight, it would surely appear in specimens taken from
such widely different sources. This conclusion still remains in
force even supposing there be a constant error in the process, for
the constant error must affect all the results equally, and could not
possibly equalise unlike results.

A third conclusion pointed out by the determinations is that the
argentic nitrate was the normal compound and quite pure; for it
will be remembered that two entirely different samples had been
used in the course of the work.

There is but one point which remains to be considered, and that is
the existence or non-existence of a constant error in the reaction.
That this is by far the most important point in the whole dis-

cussion it is unnecessary to state.   Whether there be such a constant error, future investigations may show ; for the present it is sufficient to say that it is extremely difficult to see where such an error might creep in.   The whole reaction is so simple and so sharp that the probability of error is reduced to a minimum, and in every case any possible cause of error has been guarded against.

Professor Cooke, under whose direction the whole investigation has been conducted, suggested that similar experiments be made, using argentic sulphate instead of the nitrate ; but after a large number of trials this was found to be impracticable : first, because the solution has a much higher freezing point than that of the nitrate ; and secondly, because the solution was necessarily so dilute, on account of the slight solubility of argentic sulphate, that the complete precipitation of the silver required a much longer time, giving more opportunity for secondary reactions.   The silver was always accompanied by a very slight admixture of some basic cupric sulphate ; and hence this method, which, if successful, would have been able to throw much light on the question of a constant error in the previous results, had to be abandoned.

CAMBRIDGE, *December* 15, 1887.

LVIII.—ADDITIONAL NOTE ON THE RELATIVE VALUES OF THE ATOMIC WEIGHTS OF HYDROGEN AND OXYGEN.[1]

BY JOSIAH PARSONS COOKE AND THEODORE WILLIAM RICHARDS.

The preceding paper [2] on this subject was already in print, and a number of the extra copies had been distributed, when the writer received a letter from Lord Rayleigh, stating that he had been engaged on a similar work, and had observed that the glass balloon used in Regnault's method of weighing gas volumes, when exhausted, was sensibly condensed by the pressure of the air. Obviously, if this were true, the *tare* of the balloon thus exhausted would be too large in consequence of the lessened buoyancy of the atmosphere, and hence the subsequently observed weight of gas when the balloon was filled would be too small.   A shrinkage amounting to a single cubic centimeter would make a difference of

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] This Journal **10**, 81 ; and Proceedings American Academy of Arts and Sciences.

about 1.29 milligrams, and Lord Rayleigh suggested that our
results might have been influenced by a constant error arising from
this source.   As the same balloon represented in Figure 1 of the
preceding paper had been used in all our determinations, and was
still in good condition, there was no difficulty in determining the
amount of shrinkage under exhaustion, and thus finding the cor-
rection which ought to be applied to the results on this account.
The method we used was briefly as follows :

The balloon was first exhausted, and then completely filled with
boiled distilled water at an observed temperature.   The weight of
this water having been taken, and the internal volume of the balloon
thus determined, a small portion of the water—190 cubic centimeters
—was run out, and the volume estimated both by direct measure-
ment and also by reweighing the balloon.   With these data we
could readily calculate the volume of air left in the balloon for any
given temperature, and the small amount of water lost by evapo-
ration in the subsequent exhaustion produced no sensible effect on
the result, as a knowledge of the volume within five cubic centi-
meters was all that the present problem required, and the water
did not lose in weight more than two grams during the whole series
of experiments.

The balloon was now thoroughly exhausted, allowed to stand, and
again exhausted several times, until a vacuum gauge connected
with it remained constant over night, and indicated the calculated
tension of aqueous vapor, which showed that all the air—dissolved
or otherwise—had been practically removed.

A sufficient mass of water was left in the balloon to sink it under
water, and thus immersed in a large vessel filled with distilled water
(which had been boiled and allowed to cool), it was now suspended
from the beam of the balance used throughout this investigation.
No air bubbles formed on the glass, and care was taken to remove
all entangled air from the connecting tubes.   The weight soon
became constant, and the tare could be accurately determined
within a centigram.   The connecting tubes of the balloon were
next lifted above the surface of the water, and, after carefully
drying the inlet, the outside air was admitted, and the temperature
of the water in the tank and the height of the barometer observed.
On again immersing the balloon there was a large loss of weight—
about 1.4 grams—over six times the weight of air admitted—only
about 0.2 gram.   There had evidently been a marked shrinkage

under exhaustion amounting to about 1.6 cubic centimeters. This decrease of weight was noted after the equilibrium had become constant, usually in about five minutes.

It is probable that the admitted air was saturated with moisture, and the calculation is based upon that assumption; but this would make no practical difference in the weight so far as the problem before us is concerned. Appended is an example of the method.

SERIES I. *Determination* 2.

Tare of globe exhausted = 198.22 grams. $T° = 17.30°$.
"   "   filled   = 196.83 $T° = 17.30°$.

Observed loss of weight =   1.39

Atmospheric pressure   = 75.86 cm.
Tension of aqueous vapor = 1.46

Difference = 74.40

Weight of 188 cc. moist air at 17.3° and 74.4 cm. = .22 gram.
Observed loss of weight of globe   = 1.39

Water displaced by difference of volume = 1.61

Diff. of volume corresponding to 74.4 cm. pressure = 1.61 cc.
"   "   "   76.8 cm.[1]   "   = 1.66 cc.
Weight of 1.66 cc. of air at 76 cm. and 22° C.[1] = 1.98 mg.

Below are given the data of the two series of determinations which were made:

SERIES I.

Number.	Loss of Weight. Grams.	Atmospheric Pressure. Centimeters.	Temperature. °C.	Correction. Milligrams.
1.	1.34	76.40	18.10	1.92
2.	1.39	75.86	17.30	1.98
3.	1.39	75.80	17.32	1.98
4.	1.37	75.78	17.40	1.96
5.	1.39	75.75	17.45	1.99
				1.97

[1] 22° C. and 76 cm. pressure were the average atmospheric conditions at the times of weighing the globe in the previous determinations, and 76.8 cm. was the average difference of the pressure on the globe when exhausted and full of hydrogen.

SERIES II.

6.	1.38	75.60	14.50	1.98
7.	1.39	75.60	14.50	2.00
8.	1.39	75.58	14.60	1.99
9.	1.40	75.58	14.61	2.01
10.	1.39	75.58	14.65	1.99

<div align="right">1.99</div>

Total average, 1.98 milligrams.

The quantity 1.98 milligrams is then the correction sought, and this closely agrees with Lord Rayleigh's estimate of the value in the letter above referred to. Since in the work described in the preceding paper all the data required for the calculation were not recorded in every case, it will be impossible to apply this correction to each determination separately. But no sensible error can result if we add the correction to the average apparent weight of the hydrogen, easily calculated from the data given in the table on page 107.

The total weight of the hydrogen burnt in the sixteen determinations as observed was 6.7029 grams. Add to this sixteen times the correction, or $16 \times 0.00198 = 0.0317$, and we obtain 6.7346 grams for the corrected weight. The total weight of the water formed was 60.1687 grams. Hence we find by difference for the total weight of oxygen consumed in the combustions 53.4341 grams; and the corrected atomic weight of oxygen is $2(53.4341 \div 6.7346) = 15.869$.

The probable error of this result is no greater than that of the "Total average" given on page 107; for the value of the constant correction must be certainly known within the one fiftieth of a milligram. It is true that there are several variable elements which enter into the determination of this value, but they can all be estimated with far greater accuracy than the conditions of our problem require. We may therefore write as the present result of our work, $H : O = 1.000 : 15.869$.

Atomic weight of oxygen, 15.869 ± 0.0017.

If we compare this result with that of Dumas, as before, on page 109, we have for the complete analysis of water:

Percentage of oxygen after Dumas   .   .   . 88.864 ± 0.0044
Percentage of hydrogen after final result   . 11.193 ± 0.0011

<div align="right">100.057</div>

It would now appear that the close agreement before shown was a mere coincidence, and that there must have been a small constant error either in our own process or in that of Dumas. Where the error lies further investigation can alone determine : for although, after a careful revision of our work, we can discover no flaw, no one can be confident that such a constant error as has already appeared may not hereafter be found—and certainty can only be secured after repeated confirmations by essentially different methods. While, therefore, we feel bound to acknowledge without delay the cause of constant error which Lord Rayleigh has pointed out, we give our corrected result as subject to further revision. It has been suggested by Lord Rayleigh, in a "Preliminary Notice" of his work on the relative densities of hydrogen and oxygen, of which advance sheets have been received while writing this note, that in our combustions the hydrogen may have been imperfectly burnt, especially as towards the last of the combustion it must have been greatly diluted (but with air). We have no decisive evidence on this point ; but the whole course of our combustions assured us that this could not be the case. During the first stage of the combustion, when pure hydrogen was passing into the combustion tube, and while water was dropping into the condenser (Figure 4, page 96), there would often be several minutes—during which the larger part of the water was condensed —when no residual gas whatever would be seen to escape, and the bubbling of the gas through the sulphuric acid at the bend of the U tube made the least overflow perfectly evident. Again, the oxide of copper in the combustion tube was always reduced to a perfectly definite limit, leaving at least seven eighths of the tube in which the black oxide was apparently wholly unchanged. Further, it is not probable that an error arising from the imperfect combustion of the hydrogen would have a constant value. The unconsumed residue must vary greatly with the conditions of the experiment; and such an agreement as that exhibited by the results on page 107 could never have been obtained under such circumstances.

It seems unnecessary to add that every precaution was taken in our work which our experience could suggest, and that a great amount of labor was spent on such details which does not appear in the published results. Both the balances and weights employed were most carefully verified. The water formed by the combustion

was tested, and the dissolved air taken into account. We mention these points because they have been noticed by correspondents; but many similar details which were worked out and set one side we have not thought it necessary to describe in our paper. In writing such a paper elementary principles must be assumed.

In adopting Regnault's method for weighing the hydrogen used in our determinations, we assumed with him that the glass balloon used in the work remained practically constant, whether exhausted or filled with gas. We never questioned this assumption, not only because we had the greatest confidence in all Regnault's work, but also because we knew that he had himself carefully investigated the behavior of glass bulbs under pressure; and indeed he treats the subject fully in the paper immediately preceding his classical paper on gas density.[1] Moreover, we made with our apparatus a preliminary determination of the density of air, and obtained Regnault's number within the limits of the uncertainty in regard to the value of the force of gravity at this place. Regnault's values for the weight of one litre, not only of air, but also of nitrogen, oxygen, hydrogen, and carbonic dioxide, have been hitherto regarded as among the most trustworthy data of science. His determinations were all made by the method of counterpoise which we adopted in our work, and he used balloons of twice the volume of those we employed. When exhausted the glass must have been condensed to an even greater extent than has been shown above; but no account whatever is taken of this shrinkage. As Regnault's constants have been universally used, it is obvious that Lord Rayleigh's correction must be applied to all determinations of gas or vapor densities hitherto made, and to all atomic weight determinations of any kind which involve the calculation of the weight of a measured volume of any gas or vapor. Except, however, in the case of hydrogen, the correction will be inconsiderable.

J. P. C. CAMBRIDGE, *March* 15, 1888.

[1] Mémoires de l'Acad. Roy. des Sciences de l'Inst. de France, **21**, 106 and 121.

VIII.—ON SOURCES OF ERROR IN DETERMINATIONS OF NITROGEN BY SODA-LIME, AND MEANS FOR AVOIDING THEM.

By W. O. Atwater.

The object of this paper, which concludes a series upon the same general subject, is to describe some further experiments in this laboratory, adduce results of observations elsewhere, and mention certain conclusions that seem warranted concerning sources of error in the determination of nitrogen in protein compounds, especially those of animal origin, by soda-lime, and the means by which they may be obviated.

Leaving out of account the apparent gain of nitrogen which may come from impure soda-lime, or from obvious errors in manipulation, to be mentioned beyond, the principal sources of error involve loss of nitrogen. Among the sources of loss are :

1. Incomplete ammonification of the nitrogen.

2. Dissociation or oxidation of the ammonia formed.

3. Failure of the ammonia to be completely caught and retained by the acid solution.

Loss by Incomplete Ammonification of Nitrogen.

Four ways suggest themselves by which nitrogen may fail to be changed into the form of ammonia and may hence be lost in soda-lime determinations, namely, by :

1. Incomplete decomposition of the nitrogenous substance, part of the nitrogen remaining in the partially decomposed (charred) residue.

2. Formation of compounds, *e. g.* cyanides, which remain in the tube.

3. Escape of nitrogen in the free state.

4. Formation of volatile nitrogenous products other than ammonia, which either pass through the acid solution unabsorbed, or if absorbed, are not detected by the subsequent titration with alkali or other means used to find the amount of nitrogen in the solution.

As no especial study of the first three of these sources of loss has been made here, I need only refer to them briefly.

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To insure complete decomposition, fine pulverisation, thorough mixing with soda-lime, and heating, at sufficiently high temperature, until no charred residue remains, would seem to be the requisites. As to the fineness of pulverisation needed there seem to be differences of opinion among chemists. Ritthausen[1] and Gruber,[2] for instance, lay great stress upon it. Gruber cites comparative determinations of nitrogen in flesh in which the incorrect results fell nearly 0.9 per cent. below the correct ones, and the only difference in the conduct of the analyses was that, in the defective ones, the " Fleischpulver noch einzelne wahrnehmbare Körnchen enthielt." Johnson and Jenkins, on the other hand, say that: " Contrary to what is commonly stated, fine pulverisation of the substance to be analysed is not necessary. If the substance will pass holes of one millimeter in diameter it is fine enough. A sample of dried blood which passed through a sieve with meshes one millimeter in diameter gave 7.58 per cent. of nitrogen. A portion of the same, ground extremely fine with sand, gave 7.64 per cent. Fish-scrap passed through the same sieve gave 8.98 per cent of nitrogen; when ground with sand, 8.95 per cent. A second sample of fish, sifted as above, gave 8.69 per cent. of nitrogen. By the absolute method it yielded 8.79 per cent."[3]

The not inconsiderable experience of this laboratory confirms very decidedly the opinion last quoted. We have for a number of years used a sieve with circular apertures of one. millimeter diameter. A large number of comparisons of results obtained by the soda-lime and absolute methods, and in a considerable number of cases with that of Kjeldahl, have given results so concordant as to persuade us that particles which have passed through this sieve are fine enough.

In absence of definite statements as to the actual fineness which is regarded as desirable by those who insist upon very fine pulverisation, I am inclined to suspect that the standard adopted by . Johnson and Jenkins, and in this laboratory, would perhaps be regarded as satisfactory in respect to fineness by them and by investigators generally. Certain it is that when, as in a number of instances, we have tried to use a sieve of one half millimeter aperture, we have found the process of grinding painfully laborious and time-consuming, even with the use of a mill especially devised

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[1] Jour. prakt. Chem. **116**, 1874, p. 17.   [2] Ztschr. f. Biol. **16**, 380.
[3] Report of Conn. Agl. Expt. Station, 1878, 116.

for the purpose and exceeding in convenience all other forms which I have seen.

As to formation of cyanogen or other compounds which would be retained by combining with the bases of the soda-lime, I have been unable to find any experimental facts which would lead to the supposition that there is any considerable danger of loss in this way in the combustion of ordinary animal and vegetable substances, provided the soda-lime contains enough water, and the quantities of soda-lime and substance, temperature, and other conditions are appropriate.

Regarding the escape of free nitrogen by decomposition of such nitrogenous compounds as those in question (leaving out of account the dissociation or oxidation of ammonia formed from them), I am likewise unable to find any facts which imply special danger of loss in this way, although it might, perhaps, be feared from such observations as that of Liebermann that albumin on being heated with caustic baryta to 150° yields free nitrogen.[1] The main assurance that it does not escape to any great extent when the operation is rightly conducted, is found in the agreement of the results obtained with those obtained by other methods.

The presence of nitrates, as impurities in soda-lime or otherwise, may cause loss of nitrogen, perhaps as free nitrogen, but this is of course simply a contingency to be feared from careless work.

Loss of Nitrogen by Formation of Volatile Products other than Ammonia.

As long ago as 1860 Mulder called attention to the danger of loss by formation of volatile products which, escaping ammonification within the tube, were either not caught by the acid or, if retained, escaped determination by either titration with alkali or precipitation by platinic chloride.[2] About the same time Strecker observed that guanidine salts failed to yield all their nitrogen as ammonia with soda-lime.[3]

Ritthausen and Kreussler were unable to get more than 7.9 per cent. of nitrogen from leucine by soda-lime alone, even when the greatest care was taken to pulverise and mix it with the soda-lime, and 120 times as much soda-lime as substance was used. Adding sugar, however, they got as high as 10.43 per cent., very nearly the

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[1] Jbt. Ag. Chem. **21**, 766. See also Wanklyn and Gamgee, J. Chem. Soc. **21**, 1868, 25.
[2] Chem. Centrbl. 1861, 44.   [3] Ann. Chem. (Liebig) **118**, 1861, 161.

theoretical amount, and Ritthausen suggests that the trouble with leucine, as with other compounds, may be that volatile cleavage products are formed and pass over the soda-lime without their nitrogen being changed to ammonia.[1]

Märcker insists that aniline-like products may be given off instead of ammonia, and finds proof of this in observations that some substances, as for instance gluten and leucine, gave nearly or quite their full amount of nitrogen with platinic chloride, while there was decided loss by titration with alkali. With blood albumen and horse-flesh, however, there was a loss by titration which the platinic chloride did not amend, and which can be explained by assuming that products were formed which are not precipitated by the platinic chloride, which does precipitate aniline and kindred compounds.[2]

Among the materials in which Nowack and Seegen failed to obtain the normal quantity of nitrogen (see beyond) by soda-lime was barium kynurenate. Gruber very aptly remarks that as kynurenic acid has been shown to be a derivative of quinoline, the failure may have been due to distillation of the latter.[3]

E. Salkowski suggests that in determinations of albuminoids by soda-lime, bases of the pyridine series may be formed and escape ammonification. He also suggests that a substance with red color which he obtained in burning at low heat with a small quantity of soda-lime may perhaps be the chromogen of urobilin.[4]

Kjeldahl in the discussion of his method for nitrogen determinations, referring to Mulder's advice to avoid any large amount of vacant space inside the combustion tube, states a very interesting observation of his own. In making combustions of quinine-hydrochloride with soda-lime, he found that when the soda-lime was loosely packed and shaken so as to leave a channel in the ordinary way, he obtained only about one half the nitrogen, while with the conditions in every respect the same except that the tube was well packed with soda-lime so as to leave a minimum of vacant space, he obtained practically the whole of the nitrogen as ammonia by titration. He attributes the loss in the first instance to the formation of volatile nitrogenous products which, not being brought into intimate contact with the soda-lime, escaped ammonification.[5]

[1] J. prakt. Chem. **111**, 1871, 310. [2] Archiv Physiol. (Pflüger) **8**, 1874, 207.

[3] Ztschr. f. Biol. **16**, 1880, 377. [4] Ztschr. anal. Chem. **16**, 261 and 408.

[5] Ztschr. anal. Chem. **22**, 1883, 380. See also Arnold, Ber. d. chem. Ges. **18**, 1885, 809.

The experiments cited by Mr. Ball and myself[1] in the previous article of this series bear striking testimony to the danger of loss if there is not sufficient contact between the gaseous distillation products and the heated soda-lime. In determinations of casein by our usual method (which involves close packing of the soda-lime in the tube, the use of coarse particles of soda-lime for the anterior layer, heating the anterior layer before the distillation products begin to be developed, and keeping it well heated until the combustion is finished), the whole of the nitrogen, 12.43 per cent., was obtained as ammonia. But when a channel was left in the tube (and fine soda-lime was used for the anterior layer) so that there was less contact between distillation products and heated soda-lime, the nitrogen obtained as ammonia amounted to only from 12.25 to 11.65 per cent. of the weight of the casein instead of 12.43 per cent.; that is to say, from 1.4 to 6.4 per cent. (on the average 3.3 per cent.) of the whole nitrogen escaped ammonification. When, again with the channel, the anterior layer was made shorter, 7.5 cm. instead of 12 cm., the nitrogen obtained as ammonia fell as low as 10.51 per cent., the rest, 15.4 per cent. of the whole, escaping ammonification. The average loss under these last conditions was 6.4 per cent. of the whole nitrogen. Even more striking illustrations of the failure of distillation products to be changed to ammonia are given in the experiments with strychnine described in the same article. In these but a fraction, at times very small, of the total nitrogen was obtained as ammonia, although especial effort was made to secure complete ammonification.

But little consideration of the matter is needed to show that the formation of volatile nitrogenous products which would escape ammonification by the soda-lime and detection in the acid is a very natural occurrence.

The protein compounds when subjected to destructive distillation yield a great variety of products, among which are, besides water, carbon dioxide, hydrogen sulphide, and hydrocarbons, a great variety of volatile nitrogenous compounds, including ammonia, ammonia salts of the fatty acids, amines derived from the paraffins, members of the aniline and pyridine series, pyrrol, etc., etc.[2] By heating in the presence of alkalies and other reagents a great variety of other compounds, with the rest a number of acids of the

[1] This Journal **10**, 113.
[2] See Handw. d. Chem. **2**, 1161-1173, and E. Salkowski, Ztschr. anal. Chem. **16**, 1877, 261 and 408.

fatty acid series and amido acids belonging to this and the aromatic series, among which latter are leucine and tyrosine. By the action of enzymes and microbes, products akin to the alkaloids are formed. The alkaloids break up into compounds such as were mentioned above, and numerous others including members of the quinoline series.

Now these nitrogenous products vary greatly in respect to their volatility and the ease with which they are changed to ammonia when heated in presence of soda-lime (*i. e.* of water vapor at high temperature). The specific data at hand regarding the ease with which they are ammonified are meagre. There are, however, observations bearing upon this point. For instance, Goldberg finds that some of the more complex azo-compounds, with soda-lime, yield all their nitrogen as ammonia, while the simpler ones fail to do so, part escaping.[1] There is nothing more natural than that in soda-lime combustions such volatile nitrogenous products should be formed and escape ammonification.

A fact of interest here is that some, at least, of the compounds which are most difficult to determine by soda-lime are the ones that are most readily broken up into very volatile products. Such are guanidine, kynurenic acid which may yield quinoline, leucine, and quinine and other alkaloids. It is also worth noting that some of the alkaloids, the nitrogen of which it is so difficult to transform entirely into ammonia by soda-lime, manifest a similar behavior in treatment with sulphuric acid and other reagents by Kjeldahl's method,[2] and perhaps for similar reasons.

In looking over the literature of the subject, which is quite extensive, one cannot help being impressed by the fact that certain nitrogenous compounds very frequently, and others almost uniformly, fail to yield all of their nitrogen in the form of ammonia when heated with soda-lime. Whatever may be the differences of manipulation of different experimenters, nearly all find it impossible to get all of their nitrogen in that form from such substances as leucine and some of the alkaloids. But in some cases, as for instance those of Märcker and Abesser above quoted, the nitrogen has been obtained by precipitating platinic chloride even when it was not obtained by titration. Leucine[3] is in this respect an especi-

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[1] Ber. d. chem. Ges. **25**, 46.

[2] Ztschr. anal. Chem. **22**, 1883, 379.

[3] *E. g.* Märcker and Abesser, loc. cit.; Ritthausen and Kreussler, J. prakt. Chem. **111**, 1871 ; Ritthausen, ibid. **116**, 1874, 17.

ally refractory compound, though chitin,[1] gluten-protein,[2] and, in some instances, casein[3] (milk) and peptones,[4] have given trouble in this way.

The interesting researches of Schützenberger[5] have indicated that the protein compounds (albuminoids and gelatinoids) are made up of a variety of simpler compounds, among which leucine and another, or perhaps several other compounds closely allied to it, are among the important constituents. That is to say, under the influence of various agencies the protein compounds split up into a large variety of simpler compounds, among which leucine and its congeners play an important part. That these latter might be easily formed from protein compounds in the breaking up which occurs in the ordinary heating with soda-lime is a very natural inference from the facts at hand. But from its constitution, leucine might be expected to readily be split up into volatile nitrogenous compounds. Such observations as those of Märcker and Strecker, above quoted, would seem to give reasonable assurance that it actually does so. In view of these facts it will be easy to assume that in ordinary combustions by soda-lime there is a tendency to the formation of nitrogenous distillation products such as come from leucine and analogous compounds, and which would escape ammonification.[6] Such being the case, it is easy to see how volatile nitrogenous compounds might often escape ammonification unless the greatest pains were taken to insure the most perfect contact between them and the heated soda-lime (heated water vapor), and that sometimes the ammonification might be incomplete despite the greatest care. If this be correct, the difficulty of getting all of the nitrogen of peptones into form of ammonia would accord with the fact that the peptones are products of change of the albuminoids, which change, carried further, results in the cleavage of the latter into leucine and other allied products. It would also be easy to theorise regarding the constitution of the alkali albumins and casein, and to imagine that they might like-

[1] Bütschli, Ztschr. anal. Chem. **16**, 1877, 409.

[2] Märcker and Abesser, loc. cit.; Kreussler, Landw. Vs. St. **31**, 1884, 248. See also Ritthausen, loc. cit.

[3] Lehmann, Ztschr. anal. Chem. **15**, 1876, 113; Musso, ibid. **16**, 1877, 413; Menozzi, Jsb. Agr. Chem. **21**, 1878, 474; Kreussler, loc. cit.

[4] Gruber and Feder, Ztschr. f. Biol. **16**, 1880, 381.

[5] Bull. Soc. Chim. **23–30**, 1875–1878, and Chimie Générale **131**, 407.

[6] See also Hofmann, Ann. Chem. (Liebig) **79**, 29; Wertheim, Jour. prakt. Chem. **53**, 431; Williams, loc. cit. **76**, 383; and Michael, this Journal **7**, 182, for decompositions of alkaloids and other compounds, bearing upon this question.

wise be on the way toward the process of cleavage by which leucine and its decomposition products are produced. Of course this is speculation, but it at least helps us to see how the observed facts might occur; and irrespective of any such hypotheses, the known facts are sufficient to warrant the assumption that under the influence of high heat in the presence of soda-lime, numerous volatile nitrogenous compounds might be expected to be formed, some of which would resist ammonification; and that certain classes of protein compounds would be especially prone to such decomposition, even though, in the present state of our knowledge, we are unable to say just exactly what those compounds are, or what are the processes of cleavage they go through, or what are the nitrogenous products that resist ammonification. An illustration of the difficulty of ammonifying some of these volatile compounds is found in the above mentioned case of strychnine in the experiments detailed in the previous article of this series. Neither the most painstaking effort to secure contact between the gases and the soda-lime by the Will-Varrentrapp method, nor by the greatest care in heating by that of Kjeldahl, sufficed to convert all the nitrogen into ammonia. On the other hand, the results with casein, when means were taken to secure adequate contact with soda-lime and to avoid dissociation, were most satisfactory. But when a channel was left in the tube so that the distillation products were not brought into close contact with the soda-lime, the loss was at times very large.

The lesson which all these considerations teach, and which is enforced by those cited in the previous articles, is the importance of providing intimate and sufficient contact between the distillation products and the heated soda-lime. This is done by fine pulverisation and intimate mixture of substance with soda-lime; by having the tube closely packed with soda-lime to avoid open spaces; by providing a long enough anterior layer of soda-lime, and by heating this layer well before the gases are disengaged, and keeping it well heated until the combustion is finished. At least such seems to me the just inference from the facts at hand.

Loss of Nitrogen in Distillation Products as indicated by Coloration of Acid Solution in the Nitrogen Bulb.

It is frequently urged, *e. g.* by Johnson and Jenkins,[1] that the combustions should be so conducted as to avoid any considerable

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[1] Report of Conn. Ag'l Exp't Station, 1878, 116.

discoloration of the acid solution, since the coloring matter may contain nitrogen. I have been at no little pains to learn how to insure this result. In how far it may be accomplished by the use of slaked lime, as suggested by Johnson,[1] I am unable to say, having had no experience. One of my assistants, Mr. G. P. Merrill, made, at my suggestion, a considerable number of combustions with nitrogen-free stearin at different temperatures, with varying degrees of rapidity and different lengths of anterior layers of anterior soda-lime. In general we found that the more the gaseous products of distillation in the tube were brought into contact with the soda-lime, the less was the discoloration manifested. But we were unable, even with the highest heat, very long tubes, and slow conduct of the operation, to secure a complete combustion of the distillation products; materials with the odor of hydrocarbons being always given off in considerable quantities. These and other similar experiences gave me the impression that the largest conveniently practicable contact between the gaseous products of distillation and the soda-lime was desirable, and on that account we practiced for a considerable time the use of long tubes with a long layer of soda-lime. Several circumstances, however, have shaken our faith in the need of this precaution. One is found in the comparative results of determinations with the long and the short tubes detailed in Article IV of this series,[2] in which the same quantities of nitrogen were obtained with tubes of 40 cm. and closely packed anterior layers of soda-lime of 12–15 cm., as with tubes of 60–75 cm. and correspondingly longer anterior layers. The comparative results in the combustion of ammonium sulphate in the long and short tubes, cited in the same article, seem to preclude the assumption that any loss of nitrogen from dissociation in the long tubes could have compensated for what would otherwise have been a gain from more complete ammonification. This effort to secure more perfect ammonification by means which tend to prevent the formation of colored compounds was therefore without avail. Another fact which militates against the idea that coloration of the solution necessarily indicates the presence of nitrogen compounds which have escaped ammonification, is found in the results of quite extensive experience in this laboratory, in which we have taken pains to note through a period of several months the amount of discoloration in the acid solution as measured by the eye. When we came to collate these

[1] This Journal **6**, 60.   [2] Ibid. **9**, 320.

observations, which include many scores of determinations, we found to our surprise that we had, with no exceptions exceeding the practically unavoidable variation of duplicate analyses, as much nitrogen with the considerably discolored and turbid as with the nearly clear and colorless solutions ; nor did the quantity of nitrogen average materially less in the former than the latter.

Johnson[1] mentions that in combustions with the soda-lime made from slaked lime and sodium carbonate, as suggested by himself,[2] "the acid in the bulk-tube is frequently colored more or less deeply red." On one occasion, in making some combustions with Johnson's soda-lime, we noticed that the acid in the bulb became reddish in color during the combustion. The soda-lime was a little moist. It was dried and the same combustions repeated. The solution then remained perfectly colorless. On another occasion I noticed a similar red color in the solution when moist ordinary soda-lime was used. The same soda-lime was dried and the combustions repeated. The solutions were then colorless. In each of these two cases the solution was very clear with both the moist and the dry soda-lime, and the red color with the moist soda-lime was very pronounced. What the coloring matter was I am unable to state, but the observation seems to be very similar to the one by E. Salkowski, above cited, from which he infers the presence of the chromogen of urobilin.

The following series of determinations of nitrogen in a specimen of (probably impure) albumen prepared from beef, include the observations just referred to as made with Johnson's soda-lime, and may be worth citing.

The combustions were conducted at what we have called "high heat,"[3] to wit, the highest heat the tubes of the most difficultly fusible Bohemian glass we could obtain would bear without bursting. The time of the combustions was about 60 minutes in each case. The percentages of nitrogen are calculated on water-free substance. The determinations were made by a student in this laboratory some years ago when the investigations here reported were being entered upon. The results are given in Table I.

The differences in results, which vary from 15.71 to 16.24 per cent., I presume to be due to differences in the charging of the tube. That is to say, it seems to me most probable that the low results in

[1] Loc. cit. 61.   [2] This Journal **1**, 77.
[3] See Article IV of this series, this Journal **9**, 315.

Nos. 3-8 were due to loose packing of the soda-lime in the tube, and consequent incomplete contact of distillation products with the soda-lime. I can think of no other explanation of the wide discrepancies. There is perhaps a relation beween either the clearness or the color of the solution and the apparent accuracy of the results, though it is not very pronounced.

TABLE I.

Determinations of Nitrogen in Albumin.

Number	1	2	3	4	5	6	7	8
Soda-lime . . .	Ordinary.		Johnson's.				Ordinary.	
Length of tube .	75 cm.	75 cm.	75 cm.	75 cm.	40 cm.	40 cm.	40 cm.	40 cm.
Solution . . .	Nearly clear. Colorless.		Perfectly clear. Deep red.		Somewhat turbid. Colorless.			
Per cent. N found	16.24	16.25	16.05[1]	16.07[1]	16.00	15.78	15.71	16.10

[1] Soda-lime moist.

Thus in Nos. 1 and 2 the determinations were apparently correct (though there is no proof that such was the case). The solution was colorless and had but little matter in suspension. In Nos. 3 and 4, in which the soda-lime was moist, there was no visible suspended material, but the solution was red, and less nitrogen by about 0.2 per cent. was obtained. In Nos. 5 and 6, which were duplicates of Nos. 3 and 4, except that the soda-lime was dried, the solution was colorless but somewhat turbid from suspended matters, and still less nitrogen was obtained. In Nos. 7 and 8, which were duplicates of Nos. 1 and 2, except that the tubes of the latter were of extra length, the solution was somewhat turbid and the percentages of nitrogen were small.

When these results were obtained we were inclined to interpret them as confirming the idea that turbidity and color in the solution implied loss of nitrogen. But perhaps all that they amount to is to furnish illustrations of the general facts that neither agreement of duplicates (compare 1 and 2 with 3 and 4) nor the clearness or turbidity, nor the presence or absence of color of the solutions, can be taken as a test of the correctness or incorrectness of the determinations.

Although we were somewhat surprised to find, in comparing the large number of results referred to above, that the nitrogen obtained where the solutions were nearly clear and colorless averaged just about the same as where they were more turbid or colored, yet it is after all not so strange, in view of the facts that :

(1). Non-nitrogenous materials, such as the decomposition products of fats and carbohydrates, and probably the non-nitrogenous cleavage products of protein compounds as well, may impart turbidity and color to the solution. That is to say, neither color nor turbidity is at all an evidence of presence of nitrogenous matters.

(2). Even if the color be due to nitrogen compounds, it does not by any means prove the presence of enough to have any material effect upon the result, since the quantity which would color a small amount of solution might easily be far too slight to be revealed by titration.

(3). Many volatile nitrogenous compounds such as we should expect to escape ammonification in soda-lime combustions, *e. g.* amido acids and amines, are colorless and soluble. Hence absence of turbidity or color is no proof of absence of non-ammonified nitrogen compounds.

I do not by any means mean that turbidity and color are not to be avoided if practicable, or that they do not indicate imperfect combustion. What I wish to urge is, that neither color nor turbidity, unless excessive, is an indication of a bad, or their absence a proof of a good determination.

The danger of loss of nitrogen through oxidation by nitrates occurring in the soda-lime as impurities, or introduced with the substance to be analysed, requires no discussion here.

What has been urged regarding incomplete ammonification of nitrogen of protein compounds may be briefly recapitulated as follows :

(1). Loss by incomplete decomposition would seem to be best prevented by fine pulverisation of substance, thorough mixing with plenty of soda-lime, and heating until no considerable amount of charred residue is left.

(2). Loss by formation of cyanides which combine with the bases of the soda-lime, does not seem to occur if the substance is mixed with enough soda-lime of proper water content and properly heated. Comparison of results of properly conducted combus-

tions with those obtained by other methods implies no considerable escape of nitrogen in the free state.

(3). There is great danger of loss of nitrogen in volatile distillation products which escape ammonification. With some compounds, as alkaloids and leucine, this seems extremely difficult to avoid; but with the ordinary protein compounds of animal and vegetable tissues, and with the casein of milk, the experience of this laboratory implies that complete ammonification can be insured by providing for sufficient contact of the substance and its decomposition products with heated soda-lime, (*i. e.* with water vapor at high temperature).

(4). This needed contact is best secured by (*a*) thorough mixing of substance with soda-lime; (*b*) use of soda-lime which contains a rather large proportion of lime, is not too fusible and does not shrink too much in heating; (*c*) carefully avoiding a channel; (*d*) providing a considerable anterior layer of soda-lime; (*e*) heating this latter to dull redness before bringing the heat to bear upon the substance, and keeping it hot until the combustion is done.

(5). While it is desirable to avoid the escape of matters which color the acid solution in the nitrogen bulb and render it turbid, the presence of these is not an indication of incomplete, nor their absence an indication of complete ammonification of the nitrogen.

XXXVII.—ON THE ACTION OF SILICON TETRA-FLUORIDE ON ACETONE.

By T. H. Norton and J. H. Westenhoff.

Among the few typical inorganic compounds whose reactions with organic substances have either been entirely neglected or but slightly studied, silicon tetrafluoride is probably the most important.[1]

[1] After the completion of most of the work described in the present paper, Prof. C. L. Jackson and A. Comey published a note in the Berichte der deutschen chemischen Gesellschaft (**19**, 3194), in which they describe the action of silicon fluoride on aniline, giving rise to the compound $(C_6H_5NH_2)_3(SiF_4)_2$. Prof. Jackson has courteously informed us that their investigation would be, at least for the present, confined to the study of the reactions of the fluoride with amines, and that the examination of the reactions with oxygen compounds lay open to us.

With the intention of examining the action of the fluoride on several classes of compounds, we have studied first its reaction with acetone. This was chosen on account of the readiness with which acetone enters into reaction with almost all of the reagents employed in organic chemistry.[1]

The silicon fluoride used in the reaction was generated by gently heating on a sand-bath, in an ordinary bottle of thick glass, a mixture of finely powdered fluorspar, finely powdered glass, and sulphuric acid. The current of gas was passed slowly into 825 grams of acetone (boiling point 56°–58°) kept at 0°. The liquid, shortly after the entrance of the gas, assumed a dark color, which increased in intensity as the operation continued. When the absorption seemed complete the evolution of gas was stopped, and it was found that the 825 grams of acetone had absorbed 375 grams of silicon fluoride, or 45.3 per cent. of its weight. The dark colored product thus obtained gave off vapors of SiF_4 freely when exposed to the air. A very slight amount of silicic acid was deposited during the process of absorption.

The liquid was first heated in a flask provided with an inverted condenser for the purpose of removing the excess of fluoride absorbed. In a short time it underwent a loss in weight of 100 grams. There remained 1100 grams of the liquid, and this was next subjected to distillation. The distillate weighed 600 grams, and 435 grams of a tarry residue remained in the retort. The clear liquid obtained by this means was next subjected to a series of seven fractional distillations. Tarry residues remained in the distilling flask after each series of distillations, 25 grams after the first series and an average of 9 grams after each of the other series. During each of the seven series of distillations there was likewise an average loss of 22 grams, due apparently to the liberation of SiF_4.

The seventh fractionation gave the following results :

Fraction boiling at	
56°–60°	199 grams.
60°–65°	58
65°–70°	27
70°–80°	19
80°–90°	14
90°–100°, A	73
90°–100°, B	50

[1] Compare more especially Landolph, Ber. d. chem. Ges. 12, 1579, action of boron trifluoride on acetone.

Of these fractions the one distilling at 56°-60° was naturally nearly pure acetone. The smaller fractions between 60° and 90° were colorless when distilled, but in an hour or two assumed a dark brown hue, indicating the presence of unstable compounds, and consequently of rapid decomposition. Two fractions boiling between 90° and 100° were obtained—A, a liquid lighter than water, and B a liquid heavier than water. These fractions were non-miscible.

The following are the specific gravities of the different fractions:

56°–60°	0.818	80°–90°	0.942
60°–65°	0.851	90°–100°, A	0.904
65°–70°	0.873	90°–100°, B	1.36
70°–80°	0.898		

The fraction A was slightly unstable, the colorless liquid darkening gradually on standing, although in a much less marked degree than was the case with the fractions obtained at lower temperatures. Silicic acid also separated out in the form of a gelatinous mass when the liquid was allowed to stand for some time. It seemed to contain no fluorine, for, on heating with sulphuric acid and passing the vapors through water, no separation of silicic acid took place, as is the case when vapors of silicon fluoride come in contact with water.

The fraction B was of a light yellow color, and was the only product of the distillation not subject to a more or less rapid change in coloration.

These two products were the only ones subjected to analysis. The lower fractions were not only of comparatively slight amount, but also too unstable to offer any hope of satisfactory analytical results.

Analysis of the fraction A.—The combustions were made with lead chromate.

I. 0.1089 gram of substance gave 0.1072 gram of H_2O, equal to 0.0119 gram of H or 10.92 per cent.; and 0.2538 gram of CO_2, equal to 0.0690 gram of C, or 62.71 per cent.

II. 0.2927 gram of substance gave 0.3024 gram of H_2O, equal to 0.0336 gram of H, or 11.7 per cent.; and 0.6687 gram of CO_2, equal to 0.1824 gram of C, or 62.3 per cent.

The silicon was determined by treating the liquid with a concentrated solution of caustic potash, acidifying with hydrochloric

acid, and following out the ordinary method for the determination of silica.

I. 1.1984 grams of substance gave 0.061 gram of SiO_2, equal to 0.028 gram of Si, or 1.44 per cent.

II. 1.12 grams of substance gave 0.0383 gram of SiO_2, equal to 0.0178 gram of Si, or 1.33 per cent.

Polis[1] gives a method of determining silicon in organic compounds which consists essentially in dissolving the substance in warm sulphuric acid and then adding a concentrated solution of potassium permanganate to complete oxidation. This method was also used with the following result:

III. 0.7718 gram of substance gave 0.0465 gram of SiO_2, equal to 0.0217 gram of Si, or 2.63 per cent.

	I.	Found. II.	III.
H	10.92	11.7	...
C	62.71	62.3	...
Si	1.44	1.33	2.63

Analysis of the fraction B :

I. 0.2532 gram of substance burnt with lead chromate gave 0.2309 gram of H_2O, equal to 0.0256 gram of H, or 10.11 per cent. ; and 0.0927 gram of CO_2, equal to 0.0255 gram of C, or 10.07 per cent.

II. 3.318 grams of substance gave on treatment with caustic potash 0.3979 gram of SiO_2, equal to 0.1855 gram of Si, or 5.55 per cent.

III. 2.7146 grams of substance gave by the same method 0.3138 gram of SiO_2, equal to 0.1463 gram of Si, or 5.39 per cent.

IV. 0.7168 gram gave on treatment with permanganate 0.011 gram of SiO_2, or 0.0051 gram of Si, equal to 0.714 per cent. (This method of Polis was evidently not adapted to the analysis of this substance, as silicon fluoride was evolved in notable quantity on the addition of the sulphuric acid.)

	I.	Found. II.
H	10.11	...
C	10.07	...
Si	5.55	5.39

It was observed in the above mentioned combustion that a slight deposition of silicic acid took place in the calcium chloride tube

[1] Ber. d. chem. Ges. **19**, 1024.

used for the absorption of water, resulting undoubtedly from the liberation of silicon fluoride during the operation and its decomposition by the moisture gathered in the tube. The percentages for hydrogen are therefore higher than the truth. An element of uncertainty also exists with regard to the silica determinations, especially in the presence of fluorine.

The analytical data are exceedingly unsatisfactory, giving but little clue to the probable composition of the two products.

In fraction A the analyses would indicate the presence of about 25 per cent. of oxygen, as there seemed to be no fluorine in this product. The percentage of carbon in this liquid corresponds very closely to the percentage of carbon in acetone, and it apparently is a compound of acetone with a very small amount of silicon or silica.

In fraction B the small amount of carbon, the larger amount of silicon, and the fact that about 75 per cent. of the liquid consists of oxygen and fluorine in unknown proportions, render it impossible to make any supposition with regard to the probable composition of the substance which seems to be the most stable and the most important product of the reaction.

The total absence of a method for determining fluorine in organic substances brings such an element of uncertainty into the examination of a compound containing both fluorine and oxygen that we have continued the investigation no further in the direction indicated, feeling that much more satisfactory work can be accomplished by confining ourselves to the study of the reactions of silicon fluoride with non-oxygenated bodies.

XXXVIII.—ON THE LIMITS OF THE BROMINATION OF ACETONE AT 0°, AND ON THE ACTION OF AMMONIUM SULPHOCYANIDE ON MONOBROM-ACETONE.

BY T. H. NORTON AND J. H. WESTENHOFF.

The direct action of bromine on acetone has been studied by Linnemann,[1] Emmerling and Wagner,[2] and Mulder.[3] The first states that on mixing the two at 0° he obtained an addition product, $C_3H_6O.Br_2$, in company with epibromhydrine, and acroleïn

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[1] Ann. Chem. **125**, 307. [2] Ibid. **204**, 89. [3] J. prakt. Chem. **91**, 475.

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compounds. Emmerling and Wagner prepared monobromacetone by passing a current of air saturated with bromine vapors through ice-cold acetone. Mulder obtained a tetrabromacetone and a pentabromacetone by adding a large amount of bromine to acetone kept at or below 0°. As neither Linnemann nor Mulder gives analytical data, and Linnemann gives also no description of the physical properties of his additive product, it seemed of interest to us to determine the limits within which bromine can be directly substituted for hydrogen in the acetone molecule at a low temperature. At the same time we wished to see whether it would be possible to prepare directly the unsymmetrical dibromacetone which Sokolowsky[1] obtained by allowing two molecules of bromine to act on acetone in very dilute aqueous solution.

For this purpose 100 grams of acetone were placed in a flask surrounded by crushed ice, and 235 grams of bromine were slowly added. The product was then thoroughly washed with water to remove the hydrobromic acid formed, and dried over calcium chloride. It weighed 248 grams, was of a reddish brown color, and possessed a specific gravity of 2.1. (The specific gravity of monobromacetone is 1.99, and that of unsymmetrical dibromacetone 2.5.)

This product was treated again with bromine, 100 grams being added under the observance of the same precautions. After washing and drying the liquid resulting from the second treatment, we found that there was no noticeable change in the color, but that the specific gravity had risen to 2.35. The same process was repeated and 100 grams of bromine were again introduced. After this third addition a notable amount of free bromine was present in the liquid, which had not hitherto been the case. During the washing of this product in order to remove the free bromine and hydrobromic acid, the volume was at first but little changed. After a short time it diminished rapidly with each subsequent washing. The final product had a deep red color, and possessed a specific gravity of but 2.2. The odor of free bromine was quite noticeable after it had been allowed to stand for a short time.

Judging from these results it would seem to be impossible to convert acetone entirely into a product containing more than one atom of bromine by the direct addition of bromine at a low temperature,

[1] Jour. of the Russian Chem. Soc. **8,** 330.

although the specific gravities would indicate that we obtained a mixture of monobromacetone and dibromacetone containing over 50 per cent. of the latter compound. There appears to be a certain limit to the action of the bromine beyond which rapid decomposition sets in, as seen above. In the case of chlorine, on the contrary, it is possible to substitute from one to five atoms of hydrogen in acetone by the direct action of the halogen.

We could obtain no trace of the additive product mentioned by Linnemann. His description of this substance is exceedingly meagre. He states that it results from the addition of ice-cold bromine to cold acetone, that it is exceedingly unstable, decomposing at ordinary temperatures with separation of hydrobromic acid and giving off the odor of acroleïn. The same decomposition occurs on distillation, vapors of hydrobromic acid being driven off and the distillate showing every property of acroleïn.

We find, on the contrary, while carrying out the experiment under the same conditions, that the reaction is not additive, but purely one of substitution. The bromine replaces hydrogen, hydrobromic acid is formed, and the crude product is simply the mixture of the two substances, a brominated aceton and hydrobromic acid, from which the latter constituent is removed at once by washing. As it is well known that monobromacetone as obtained by other methods is quite susceptible of decomposition, especially when not pure, *i. e.* not freed from the acid formed during the reaction, and also that on distillation it yields products similar to those described by Linnemann, we surmise that the substance supposed by the latter to be $C_2H_6O.Br_2$ was simply the mixture of the two products of the reaction $C_3H_6O + Br_2 = C_3H_5BrO + HBr$, not yet freed from the acid by washing. The absence of analytical data and any description of physical properties in Linnemann's account prevents us from offering more than a surmise.

Action of Ammonium Sulphocyanide on Monobromacetone.— Monochloracetone and ammonium sulphocyanide act upon each other with ease in an alcoholic solution, the product of the reaction being the sulphocyanide of sulphocyanpropimine:[1]

$$C_3H_5ClO + 2NH_4SCN = \begin{array}{c} CH_2SCN \\ | \\ CNH.HSCN \\ | \\ CH_3 \end{array} + NH_4Cl + H_2O.$$
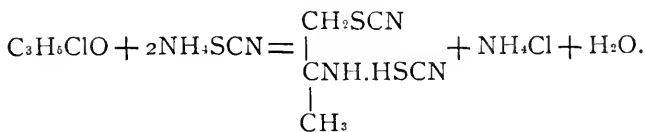
[1] Tcherniac and Norton, Ber. d. chem. Ges. **16**, 345.

As the corresponding bromine derivative of acetone is more easily prepared than its chlorine homologue, it seemed of interest to us to ascertain whether it was capable of replacing monochloracetone in the above mentioned reaction.

The monobromacetone used was prepared according to the method indicated by Emmerling and Wagner,[1] which consists in conducting a current of air laden with bromine vapors through ice-cold acetone. 100 grams of acetone and 138 grams of bromine gave 110 grams of monobromacetone after thorough washing and drying over calcium chloride. This product had a specific gravity of 1.99, and the analysis gave 58.10 per cent. of bromine (the theory requires 58.45).

The method used in the preparation of sulphocyanpropimine from monochloracetone was followed in the treatment of the bromine compound. 15.5 grams of ammonium sulphocyanide were dissolved in 93 grams of 90 per cent. alcohol. The equivalent amount of monobromacetone—14 grams—was then added, and the mixture was kept at a gentle heat for over a day, during which time ammonium bromide continued to separate out.

The alcoholic solution, which had assumed a deep red tint, was then filtered from the residual ammonium bromide and evaporated to dryness on the water-bath. The dark residue obtained by this means was treated with four times its weight of water and allowed to stand for three days. The resultant yellow solution was separated from a black tarry residue and carefully examined. It was found to contain some ammonium bromide and ammonium sulphocyanide with a small amount of coloring matter, but no trace of sulphocyanpropimine sulphocyanide could be detected. The operation was repeated several times, but in all cases with equally fruitless results.

It seems probable, therefore, that while a certain amount of sulphocyanacetone, $CH_3CO.CH_2SCN$, may be formed, as is evident from the amount of ammonium bromide produced, the monobromacetone is not susceptible of change into the corresponding imine.

[1] Ann. Chem. **204**, 28.

XXXIX.—ON THE ACTION OF CHLORINE ON ACENAPHTHENE.

By J. T. Kebler and T. H. Norton.

The only halogen derivatives of acenaphthene thus far known are bromacenapththene, $C_{12}H_9Br$, dibromacenaphthene, $C_{12}H_8Br_2$, and dibromacenaphthene bromide, $C_{12}H_8Br_2.Br_4$; all of which are obtained in well defined crystalline forms. We have submitted this hydrocarbon to the action of chlorine in the hope of increasing the small number of acenaphthene derivatives. The operation was conducted in the following manner: Acenaphthene (melting point 95°) was introduced, in portions of 50 grams, into a U tube connected with a chlorine generator. A current of chlorine, well washed and perfectly dry, was passed through the hydrocarbon until no further increase of weight could be obtained. The acenaphthene was attacked at once, even at ordinary temperatures, began immediately to liquefy, and considerable heat was evolved, while large amounts of hydrochloric acid gas were given off, indicating that the reaction was one of substitution and not addition. The color of the liquid, at first of a light straw tint, gradually grew darker as the action of the chlorine progressed. After the absorption of a considerable amount of chlorine, the straw-colored liquid possesses interesting fluorescent properties, the reflected rays being of a deep blue color. This property is gradually lost as the operation continues, and disappears completely at the point of complete saturation. The liquid contents of the tube possessed at first the consistency of rich cream. As the absorption progressed the fluidity diminished, until towards the end it was necessary to keep the U tube in boiling water in order to permit the passage of the chlorine gas. By this means the hydrochloric acid formed in the reaction was likewise completely driven off.

The product of this chlorination is a light brown syrup which at 12° is so viscous that it can be poured only with difficulty, while at 25° it is quite liquid. It is by no means stable. In contact with water or when slightly moist it decomposes very rapidly, and even when tightly corked in a perfectly dry bottle, a slow decomposition accompanied by an evolution of hydrochloric acid gas is maintained. During this process of alteration the color changes to a dirty white, beginning at the surface and gradually extending throughout the mass. It is entirely insoluble in water,

but dissolves readily in hot alcohol, ether, benzene, and carbon disulphide. Attempts were made to obtain crystalline products from the various solutions, but without success. The specific gravity was found to be 1.43 at 17°. When heated on porcelain it becomes quite fluid; white fumes and, later, dark fumes without acid reaction are given off. It burns, but is incapable of continued combustion unless kept close to a flame. When exposed to distillation hydrochloric acid vapors are first given off, and then heavy white non-condensible vapors are evolved in company with liquid distillates. Each successive series of distillations gives products of lighter color and a less viscous nature. No considerable fractions of fixed boiling point could, however, be isolated.

Although the nature of this product was not such as to offer much hope of its being a well defined compound in a state of purity, it was submitted to analysis with the following results:

I. 0.7755 gram of substance, after combustion with lime, gave 1.3757 grams of silver chloride, equal to 0.3403 gram of chlorine, or 43.88 per cent.

II. 0.6657 gram of substance gave 1.1714 grams of silver chloride, equal to 0.2897 gram of chlorine, or 43.53 per cent.

III. 0.5387 gram of substance gave 0.9308 gram of silver chloride, equal to 0.2302 gram of chlorine, or 42.74 per cent.

These analyses were made in succession, the first immediately after the preparation of the substance, the others at intervals of three days. The constant diminution of the percentage of chlorine shows the rapidity of decomposition.

IV. 0.3341 gram of substance gave on combustion with lead chromate 0.653 gram of CO_2, equal to 0.1781 gram of C, or 53.31 per cent.; and 0.0842 gram of H_2O, equal to 0.0093 gram of H, or 2.8 per cent.

	Found.	Calculated for $C_{12}H_7Cl_3$.
C	53.31	55.92
H	2.80	2.72
Cl	43.88	41.36
	99.99	100.00

The composition approximates to that of a trichloracenaphthene, and the analytical results are only of value as showing that that compound would probably represent the limits to be reached by the direct chlorination of acenaphthene at temperatures below 100°.

XL.—ON THE URANATES OF AMMONIUM AND OF CERTAIN AMINES.

By A. I. Carson and T. H. Norton.

The literature of uranium shows that uranates of the metallic bases of normal composition, with the exception of the potassium, sodium, and lithium uranates, as prepared by the ingenious method of Zimmermann,[1] are exceedingly rare. The analyses almost invariably show more or less notable deviations in the amount of uranium present from that prescribed by theory. These deviations are in the case of the ammonium salt 1.5 per cent., barium salt 1.2 per cent., lead salt 1 per cent., and silver salt 3 per cent., while in all other cases there is not even an approximation to the theoretical composition.

The following preparations were made in the view of ascertaining the possibility of obtaining salts of more normal composition with representative organic bases.

Ammonium Uranate.—We deemed it well in this connection to first prepare and analyse this salt before passing to the study of the compounds with the substituted ammonias. Two samples were prepared, both by the addition of ammonia to an aqueous solution of uranium nitrate. The light yellow precipitate, which forms at once, was thoroughly washed and dried at 100°. The analysis of this salt, as well as of the other salts to be described, was exceedingly simple. Weighed amounts of the salt dried to constant weight at 100° were gently ignited, and changed into the green oxide of uranium, U_3O_8. In a few cases, which will be noted, the black oxide of uranium, U_2O_5, was obtained. (The first mentioned contains 84.9 per cent. of uranium, the second 85.7 per cent.)

Analyses:

	Calculated for $(NH_4)_2U_2O_7$.	First Sample. I.	II.	Found. Second Sample.
U	76.43	72.90	72.92	74.19

The results show not only an abnormal but also variable composition. Peligot found 75 per cent. of uranium in a sample of this salt.

Uranates of the Amines of the Fatty Series.—In their preparation the amines, either in the pure state or in 33 per cent. aqueous solution, were added to the aqueous solution of uranium nitrate.

[1] Ann. Chem. (Liebig) **213**, 291.

The precipitates obtained were amorphous, insoluble, of a sticky gelatinous nature, and ranged in color from light yellow to orange. They were thoroughly washed by decantation and filtration, dried to constant weight at 100°, and analysed by the same method as given in the case of ammonium uranate. During desiccation the color always deepened. When dry they could easily be powdered.

Methylamine Uranate.—The color is of a bright canary yellow. Two different samples were prepared. The analyses gave :

	Calculated for $U_2O_7(NH_3CH_3)_2$.	Found in Samples. I.	II.
U	73.17	74.13	72.54

Variable and abnormal composition was also here evident. Ignition of the first sample gave the black oxide, of the second the green oxide.

Dimethylamine Uranate.—Color a bright canary yellow. Two analyses were made from the same preparation. Each gave on ignition the green oxide.

	Calculated for $U_2O_7[NH_2(CH_3)_2]_2$.	Found. I.	II.
U	70.17	74.27	74.25

The abnormal composition is quite evident.

Trimethylamine Uranate.—Same color as the preceding compound. Two analyses were made from the same preparation. In each case the green oxide was obtained.

	Calculated for $U_2O_7[NH(CH_3)_3]_2$.	Found. I.	II.
U	67.41	71.23	71.11

The discrepancy is here still more striking.

Ethylamine Uranate.—The color is a yellowish orange. Two analyses were made of the same preparation. The black oxide was obtained in each case.

	Calculated for $U_2O_7(NH_3C_2H_5)_2$.	Found. I.	II.
U	70.17	69.90	70.17

This is the only case in which a practically normal salt was obtained.

Diethylamine Uranate.—The color was light orange. Two analyses of the same preparation gave :

	Calculated for $U_2O_7[NH_2(C_2H_5)_2]_2$.	Found. I.	II.
U	64.86	61.21	61.24

The black oxide was obtained in each case. The variation is marked.

Triethylamine Uranate.—Yellowish brown color. Two analyses of the same preparation gave :

	Calculated for $U_2O_7[NH(C_2H_5)_3]_2$.	Found. I.	II.
U	60.30	63.13	62.60

The black oxide was obtained in each case. Variation as in the preceding case.

Isobutylamine Uranate.—Color light orange. Two preparations were made. The analyses gave :

	Calculated for $U_2O_7(NH_3C_4H_9)_2$.	Found. Sample 1. I.	II.	Sample 2. III.
U	64.86	69.41	72.57	71.88

This salt shows the most striking case of abnormal and variable composition. The first sample gave the black oxide, the second the green oxide on ignition.

As will be seen from the above analytical results, the uranates of the amines of the fatty series can, as a class, lay but little claim to normal or constant composition; the greatest variations being noted in the compounds containing the largest amount of carbon.

Uranates of the Aromatic Amines.—While the addition of aromatic amines causes a precipitation in solutions of uranium nitrate, the products thus obtained seem to be of an exceedingly unstable nature, decomposition setting in almost immediately on precipitation. Three preparations of an aniline salt were attempted. In the first case aniline was added to an aqueous solution of uranium nitrate; in the other two cases it was added to an ethereal solution of the salt dried over calcium chloride. All three products resembled in color ordinary green uranium oxide. The analyses of the three samples gave :

	Calculated for $U_2O_7(NH_3C_6H_5)_2$:	I.	Found. II.	III.
U	61.54	78.56	40.27	51.41.

The first preparation gave on ignition the green oxide, the other two the black oxide. Toluidine gave equally unsatisfactory results.

XLI.—ON SOME NEW NITROPRUSSIDES.

By T. H. Norton.

The two following salts have been prepared and studied in this laboratory by Carrie E. Joslin.

Cadmium Nitroprusside, $CdFeCy_5NO$.—This salt is obtained in the form of an amorphous flesh-colored powder on the addition of cadmium nitrate solution to a concentrated solution of potassium nitroprusside. It is insoluble in water; concentrated hydrochloric acid dissolves it readily, yielding a garnet-colored solution. Long continued boiling with both dilute and concentrated nitric acid does not affect it. It is likewise not attacked by ammonia or caustic alkalies. Exposure to light and air causes no perceptible change. It possesses a specific gravity of 2.06 at 17° and is decomposed at 290°. The analysis was made by decomposing with boiling sulphuric acid, estimating the cadmium as cadmium sulphide, and estimating the iron as ferric oxide.

I. 0.8109 gram of the salt dried to constant weight at 115° gave 0.3083 gram of CdS, equal to 0.312 gram of Cd, or 34.33 per cent.; and 0.1928 gram of Fe_2O_3, equal to 0.135 gram of Fe, or 16.65 per cent.

II. 1.0353 grams of the salt dried to constant weight at 115° gave 0.4528 gram of CdS, equal to 0.3522 gram of Cd, or 34.02 per cent.; and 0.2491 gram of Fe_2O_3, equal to 0.1744 gram of Fe, or 16.85 per cent.

	Calculated for $CdFeCy_6NO$.	Found. I.	II.
Cd	34.12	34.33	34.02
Fe	17.06	16.65	16.85

Mercurous Nitroprusside, Hg_2FeCy_5NO.—This compound is obtained in the form of a pink-colored amorphous precipitate on adding a solution of mercurous nitrate to a solution of potassium nitroprusside. Its specific gravity is 3.9 at 17°. It is far from stable, being gradually decomposed by the action of air and of light. At 90° it assumes a grayish color, and at 120° it becomes perfectly black.

The method of analysis was similar to that of the cadmium salt.

I. 0.3435 gram of the salt dried to constant weight at 40° gave 0.2579 gram of HgS, equal to 0.2223 gram of Hg, or 64.71 per cent.; and 0.046 gram of Fe_2O_3, equal to 0.0322 gram of Fe, or 9.37 per cent.

	Calculated for Hg_2FeCy_5NO.	Found.
Hg	64.93	64.71
Fe	9.08	9.37

The following two salts have been prepared and examined by C. F. Windisch:

Cobalt Nitroprusside, $CoFeCy_5NO$.—This salt was precipitated on the addition of cobalt sulphate solution to a concentrated solution of sodium nitroprusside in the form of a finely divided, almost crystalline powder of a delicate pink color. The salt thus obtained is in a hydrated form and loses its water at 105°, assuming a deep blue tint. It is, however, extremely hygroscopic in this state, and rapidly absorbs moisture on cooling, resuming the original pink color. It is entirely decomposed at 170°. The compound is quite unstable, and for this reason, as well as on account of the hygroscopic nature of the anhydrous salt, it was impossible to obtain perfectly satisfactory analytical results. Two water determinations made by heating the salt dried at 40° to 105° gave 18.98 and 18.79 per cent. of H_2O. The formula $CoFeCy_5NO + 4H_2O$ would require 20.7 per cent.

An analysis of the anhydrous salt, made as soon as possible after its preparation, gave:

	Calculated for $CoFeCy_5NO$.	Found.
Co	21.40	23.37
Fe	20.38	23.20

Decomposition proceeds very steadily, as shown by the following analyses made at successive intervals of a week:

	I.	II.	III.
Co	26.20	28.62	30.06
Fe	24.66	28.19	29.44

Nickel Nitroprusside, $NiFeCy_5NO$.—The preparation of this salt is similar to that of the cobalt salt. It is obtained in the hydrated form as a dirty gray powder. Constant water determination could not be obtained. At 105° it loses water and assumes a dark green color. The anhydrous salt absorbs moisture with avidity and resumes its original gray color. At 160° complete decomposition occurs. Under ordinary circumstances decomposition likewise takes place, and analytical results were rendered unsatisfactory from this cause and from the extreme hygroscopic nature of the anhydrous salt. An analysis made shortly after the preparation gave:

	Calculated for NiFeCy₅NO.	Found.
Ni	21.40	19.83
Fe	20.38	19.53

An analysis made a few weeks later gave :

Ni	24.48
Fe	23.25

XLII.—ANALYSIS OF LOCKPORT SANDSTONE.

By H. W. WELD.

The so-called Medina sandstone has long enjoyed a high reputation as a building stone on account of the fineness of its texture and the delicacy of its coloring, qualities which have led to its use in the construction of prominent structures in many parts of the country. I am indebted for a sample of this sandstone to the courtesy of Mr. Charles Whitmore, proprietor of the important quarry at Lockport, N. Y., where the choicest varieties of the Medina stratum are obtained.

The analysis yielded the following results :

	I.	II.
SiO_2	96.31	96.52
Fe_2O_3	0.70	0.70
Al_2O_3	1.71	1.60
CaO	0.99	1.05
	99.71	99.87

No moisture was present.

The high percentage of silica and the small amount of cementing material are worthy of note as of comparatively rare occurrence. Bornemann[1] found sandstones in the Hartz mountains containing from 96.68 to 98.47 per cent. of silica. Haas[2] gives analyses of Bohemian sandstones containing from 90.55 to 93.33 per cent. of silica. Other recorded analyses of sandstones approaching so nearly the composition of pure quartz are exceedingly rare.

[1] Jahrbuch der Mineralogie, 1852, 1.   [2] Wien. Acad. Ber. (2 Abtheil.) **61**, 763-764.

ACTION OF CHLOROUS ACID UPON HEPTYLENE.

BY ROBT. G. GRISSOM.

The heptane from Pinus Sabiniana has been shown by Schorlemmer to be probably a normal heptane. The heptylene used in the following experiments was prepared from this heptane by first brominating it and then acting upon the secondary bromide formed with sodium ethylate. It was found that the best results were secured by allowing the sodium ethylate to act from twelve to twenty-four hours in the cold, and then distilling off the heptylene and alcohol together. The end of the condenser tube may dip underneath water, or better, end just above the surface of it, thus separating the alcohol from the heptylene. The latter does not seem to be soluble in water to any great extent. This heptylene was dried, redistilled, and the portion boiling at 98°–100° was used for the experiments.

The chlorous acid was formed by the action of sulphuric acid, diluted with two parts of water, on a mixture of potassium chlorate with half its weight of oxalic acid. The stream of chlorous acid mixed with carbon dioxide, thus produced, was then led into the tube containing the heptylene. To start the evolution of the gases, the small flask containing potassium chlorate and oxalic acid mixed with sulphuric acid was gently warmed by placing it in warm water. Application of cold water was used to moderate the action when necessary. Only ten or fifteen grams of potassium chlorate were used at one time. Following the directions of Domac,[1] the heptylene (about 110 grams) was placed in four tall test tubes so that each was about half full. These were properly connected with the flask for generating the gases and were surrounded by ice-water. The gas delivering tube ended just above the surface of the heptylene, thus adopting Domac's precaution, so as to avoid the troublesome explosions. To make the absorption as regular as possible, the position of the tubes with reference to the generating flask was regularly changed. The absorption was rapid, the

[1] Ann. Chem. **213**, 125.

heptylene going through various changes of color from yellow to a deep orange-brown. When the deeper color was reached the tubes were disconnected from the generating flask and placed in direct sunlight until the orange color was lost. If taken from ice water the heptylene became very warm and a rapid evolution of gas took place. It was much the best, and tended to prevent a complication of reactions, to keep the tubes all the time at a low temperature, and to shade them even from sunlight during the passage of gas. After several days the absorption took place more slowly, and an exposure of many hours was needed for decolorisation. Even with great care explosions would take place after the heptylene was largely saturated with the gas, and about half of the heptylene was thus lost. It was necessary then to stop before complete saturation or a permanent coloration was reached. The oily liquid was thoroughly washed with water until the washings no longer had an acid reaction. This wash-water acquired a pungent, irritating odor. The remaining oil was dried over calcium chloride.

Aqueous Solution.—On examining first the water used in washing it was found strongly acid; still but little of the original liquid seemed to have gone into solution. A portion of the water was placed over sulphuric acid and on evaporation left a small residue, white, deliquescent, and somewhat oily. The main part was apparently crystallised, contained chlorine, and had the smell of acetic acid and its chlorine derivatives. The amount obtained was too small for purification or further attempt at identification. The remainder of the solution was neutralised with barium carbonate, changing from a clear liquid to a rosy flesh color. The same fruity, pungent, irritating odor was noticed. This was filtered, and after evaporation to a small bulk, the barium precipitated by sulphuric acid. After filtering again it was distilled. Three fractions were taken. The first, under 100°, gave no test for chlorine; the second, 100°–101°, contained chlorine; the third, 101°–110°, contained both chlorine and sulphuric acid, the latter coming from the slight excess used in precipitating the barium. As the first only gave promise of interesting results, it was saturated with Ag_2O, filtered, evaporated over sulphuric acid, and the thin crystalline film left was analysed. As the amount of silver found was within two per cent. of that required by silver acetate, it was concluded that the principal acid present in the aqueous solution was acetic acid. The presence of chlorine, sulphuric acid and oily impurities prevented

an examination of the other fractions for butyric or other acids, and the amount was too small to attempt to purify them.

The Oil insoluble in Water.—The oily portion after the washing and thorough drying over calcium chloride, was subjected to fractional distillation under diminished pressure. In this fractionation that part boiling below 120° was looked upon as mainly unchanged heptylene. The fraction from 120°–160° was set aside. It contained chlorine, and after attempts at reduction persistently retained it. The remaining portion was fractionated three times, yielding fractions as follows: A, 160°–173°; B, 173°–177°; C, 177°–185°; D, 185°–200°; and E, over 200°. This last fraction was quite small, the thermometer rising rapidly until only a few drops remained. None of these fractions were more than a few cc. in amount. All were at first clear, colorless liquids, but the last two rapidly darkened, even though in sealed tubes and carefully secluded from the light. Fraction B was the largest in amount (6–7 cc.), and as the thermometer rose slowly from 173°–177°, this was supposed to be the purest substance, or the nearest approach to a single chemical individual. As stated before, it was the result of three careful fractionations. It was subjected to the first and most complete examination. All of the temperatures by which these fractions are distinguished are subject to correction, due to the pressure being reduced by 100 mm. The following analyses were made of these respective fractions.

Fraction B, 173°–177°.

I. 0.3170 gram substance gave 0.2205 gram H_2O, and 0.6300 gram CO_2; or 7.73 per cent. H, and 54.19 per cent. C.

II. 0.3203 gram substance gave 0.2547 gram H_2O, and 0.6336 gram CO_2; or 8.83 per cent. H, and 53.94 per cent. C.

III. 0.4181 gram substance gave 0.3287 gram H_2O, and 0.8268 gram CO_2; or 8.73 per cent. H, and 53.93 per cent. C.

IV. 0.2785 gram substance gave 0.3139 gram AgCl; or 27.85 per cent. Cl.

V. 0.2750 gram substance gave 0.3043 gram AgCl; or 28.05 per cent. Cl.

Fraction C, 177°–185°.

VI. 0.3259 gram substance gave 0.2575 gram H_2O, and 0.6544 gram CO_2; or 8.78 per cent. H, and 54.77 per cent. C.

Fraction D, 185°–200°.

VII. 0.2642 gram substance gave 0.2087 gram H_2O, and 0.5402 gram CO_2; or 8.78 per cent. H, and 55.79 per cent. C.

Fraction E, above 200°.

VIII. 0.3165 gram substance gave 0.2513 gram H_2O, and 0.6567 gram CO_2; or 8.81 per cent. H, and 56.27 per cent. C.

IX. 0.2260 gram substance gave 0.1794 gram H_2O, and 0.4672 gram CO_2: or 8.82 per cent. H, and 56.38 per cent. C.

X. 0.2680 gram substance gave 0.255 gram AgCl; or 23.49 per cent. Cl.

The following table will show how these percentages compared with those calculated for the chlorine compounds, which suggest themselves as possibly formed during the reaction:

	B.	C.	D.	E.	$C_7H_{13}ClO$.	$C_7H_{14}Cl_2O$.	$C_7H_{14}Cl_2$.
H	8.83	8.78	8.78	8.82	8.76	7.57	8.29
C	53.94	54.77	55.79	56.38	56.60	45.45	49.76
Cl	27.85	...	...	23.49	23.85	38.31	41.94

It will be observed that while the percentage of hydrogen is about the same throughout, the percentage of carbon increases up to the last fraction E. This one approaches in all of its percentages very nearly to $C_7H_{13}ClO$. That it is free from impurity is hardly possible, as is shown by the inconstant boiling point. As to the nature of the more highly chlorinated body or bodies with which it is mixed, nothing can be determined by the analyses. From the great difficulty with which chlorine was removed, it is most probable that simple chlorides were present. Nitric acid caused complete decomposition only in the neighborhood of 200°, and nascent hydrogen failed to act. As the nature of the reduction products would throw some light on the composition of these fractions, their reduction was attempted. First iron filings and acetic acid were used, then sodium amalgam, but the chlorine was not entirely removed even after days of action. The small amounts experimented with rendered vain any attempt at separation by distilling.

To sum up the results of the action of chlorous acid upon heptylene from Pinus Sabiniana, we find acetic acid and some chlorinated solid acid formed by the oxidising action, but the main portion changed into a chlorhydrine, mixed probably with chlorides.

The ease of decomposition of the chlorous acid renders it hardly possible to limit the nature of the reaction and prevent its becoming very complex.

NEW HALOGEN COMPOUNDS OF LEAD.

Lead chlorosulphocyanide. (By R. G. GRISSOM.)—This new compound can be easily prepared by acting on lead chloride with a strong solution of potassium sulphocyanide. Freshly precipitated and recrystallised lead chloride was covered with a solution of potassium sulphocyanide in excess and allowed to stand for several days. The liquid was then poured off and the residue heated several times with boiling water until all was dissolved. This fractional solution was carried out to separate, if possible, substances of different solubility. The fractions rapidly deposited crops of crystals on cooling, but examination under the microscope showed that these crystals were identical in form. Analyses were made as follows :

0.6220 gram of substance gave 0.5730 $PbSO_4$, or 68.57 per cent. of Pb. 1.0280 grams of substance gave 0.7047 gram $PbSO_4$, or 68.55 per cent. Pb.

For chlorine and sulphocyanic acid 1.0700 grams of the substance were dissolved in water and precipitated with silver nitrate. This was filtered and treated with strong nitric acid, thus oxidising the sulphocyanide. After dilution it was again filtered. The silver chloride was burned and the sulphuric acid determined in the filtrate in the usual way.

1.0700 grams of substance yielded 0.1321 gram of AgCl, or 12.34 per cent. Cl ; and 0.8440 gram $BaSO_4$, or 19.62 per cent. CNS.

	Calculated.	Found.	
Pb_2	68.46	68.57	68.55
Cl_2	11.91	12.34	
$(CNS)_2$	19.41	19.63	

The formula for the compound then is $PbCl_2.Pb(CNS)_2$. There is no water of crystallisation, and the substance can be heated to 150° without decomposition.

The solution poured off from the original lead chlorosulphocyanide yielded mainly crystals of potassium chloride together with some unchanged potassium sulphocyanide. The potassium sul-

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phocyanide was freshly prepared and purified by frequent recrystallisation.[1]

Action of ammonium hydroxide upon lead chlorosulphocyanide.—Crystals of this salt, dried at 100° and kept several months, turn partially yellow from the formation of persulphocyanogen. Those merely dried in the air do not seem to undergo this change. Some of these air-dried crystals were covered with ordinary aqua ammonia in excess and allowed to stand for six days. The color of the crystals was slightly changed, becoming dirty yellowish white. On analysis, after drying at 100°, they were found to contain 3.08 per cent. of chlorine. Sulphocyanic acid was also present, but was not determined. Another lot, after standing for three hours, gave 5.28 per cent. of chlorine. Crystals covered in the same way with ammonia water and boiled occasionally during six hours showed on analysis 2.76 per cent. of chlorine, and gave qualitative tests for sulphocyanic acid. Others boiled in this way during three or four weeks gave but a bare opalescence with silver nitrate. Ammonium hydroxide, then, does not remove either of the radicals combined with the lead in preference to the other, but removes both at the same time, until only lead hydroxide is left. Nor do there seem to be any distinct steps of removal or regular basic compounds formed as in the case of the action of ammonium hydroxide on lead chloride and iodide.[2]

Lead bromosulphocyanide.—Lead bromide crystallised from a strong solution of potassium sulphocyanide gave slightly brownish crystals, apparently of the first system. These were dried on filter paper and then over sulphuric acid. They contained 23.05 per cent. of bromine and 16.65 per cent. CNS. Calculated for PbBrCNS, 23.02 per cent. bromine and 16.85 per cent. CNS.

Hydrobromic acid was added to the mother-liquor of these crystals, and on evaporation a crop of clumpy, indistinctly yellowish crystals was obtained. These were dried and analysed, giving 3.46 per cent. of CNS. Calculated 3.56 per cent. of CNS for 8PbBr₂. Pb(CNS)₂.

Lead iodosulphocyanide. (By B. THORP.)—The first attempt at preparing this salt was by adding the excess of potassium sulphocyanide, in solution, to freshly precipitated lead iodide. On washing

[1] As Mr. Grissom was forced to leave the work at this point and it could not be turned over to any other student in the laboratory just then, I undertook myself the examination of this and other lead compounds. A description of this work follows.

[2] Chemical News **52**, 43.

with hot water lead iodide alone crystallised out. Again sulpho-
cyanic acid was used to dissolve lead iodide, but the double com-
pound refused to form and again the iodide only crystallised out.
When equivalent amounts of lead iodide and lead chlorosulpho-
cyanide were dissolved in boiling water and allowed to crystallise,
the iodide crystallised out by itself. Lastly, lead iodide was dis-
solved in a strong solution of potassium sulphocyanide. This gave
on cooling small glistening nearly white crystals. It is interest-
ing to note in this and other cases where double compounds with
lead iodide were obtained, that at one stage of the cooling numbers
of large, distinct crystals of lead iodide would separate. On
further standing and cooling these would entirely disappear and all
the crystals would be of the double compound.

Analysis gave for this compound figures corresponding to 57.22
per cent. Pb. Calculated for $PbI_2.3Pb(CNS)_2$, 57.83 per cent. Pb.

Lead chlorocyanide.—When lead chloride crystals were covered
with a strong solution of potassium cyanide, a heavy and quite
insoluble body was formed which, on standing, rapidly changed in
color to a purplish brown. This was due to partial decomposition
and loss of hydrocyanic acid.[1] This heavy insoluble powder was
washed and then dried at 100°. The analyses gave the following
results, the CN being found by difference :

	Calculated for $2Pb(CN)_2.PbCl_2$.	Found.		
Pb	77.98	78.46	78.32	77.98
Cl	8.76	8.29	8.47	8.76
CN	13.22	13.25	13.21	13.22

Lead ferrocyanide could not be induced to crystallise with lead
chloride. It is so insoluble that few of the methods of formation
used in this research could be put into practice. On covering lead
chloride with a solution of potassium ferrocyanide, the lead gave
up its chlorine completely. The resulting lead ferrocyanide per-
sistently retained some potassium ferrocyanide. Again, when lead
ferrocyanide was boiled for some time with potassium chloride,
neither filtrate nor residue contained the desired double salt.

Lead ferrocyanide covered with ammonia water for several
weeks yields a brownish-gray white mass which was free of
ammonia and contained 12.42 per cent. of ferrocyanic acid and
.45 per cent. of ferric oxide. It is a basic ferrocyanide.

[1] Chemical News **51**, 45.

Of course the attempt to crystallise lead ferrocyanide from hydrochloric acid ended in the decomposition of the ferrocyanide with the formation of lead chloride and separation of Prussian blue.

Lead bromiodide. (By B. THORP.)—When lead iodide is dissolved in hydrobromic acid, the first crystals are of a deep yellow tint, approaching orange. The crystals on analysis yielded 49.75 per cent. Pb. Calculated for $PbBr_2.PbI_2$, Pb = 49.93 per cent. These crystals then have the composition represented by the formula $PbBr_2.PbI_2$.

The second crop of crystals have a straw-yellow color and gave 52.99 and 52.57 per cent. Pb, 30.61 per cent. Br, and 16.20 per cent. I. Calculated for $3PbBr_2.PbI_2$, 52.94 per cent. Pb, 30.77 per cent. Br, and 16.32 per cent. I.

The third crop are white in color and yield on analysis 54.19 and 54.34 per cent. Pb. The calculated percentages for a substance of the composition $6PbBr_2.PbI_2$ are = 54.34 per cent. Pb.

The fourth crop are also white, and gave only a slight reaction for iodine. They contained 56.12 per cent. Pb, and are therefore nearly pure lead bromide. In form these crystals are all alike, closely resembling ordinary lead bromide.

Lead chlorobromiodide. (By B. THORP.)—Lead chloride, lead bromide and lead iodide were dissolved together in hot water and allowed to crystallise. No special proportions were taken, though in the first experiment an excess of lead iodide was probably present. In the second, more lead bromide and lead chlorine were present, with the bromide probably in excess. In both cases the iodide crystallised out abundantly immediately on cooling. The second, third and fourth crops of crystals were taken separately. They were like one another in appearance, forming masses of long silky yellowish white needles. They combined chlorine, bromine, and iodine. Analyses of the three last fractions in the second experiment gave the following percentages of lead :

I. Pb = 60.34; II. Pb = 61.48; III. Pb = 61.32. Analysis of the fourth fraction gave, IV. Pb = 61.57.

There seems to be only one compound formed, as in I. the analysis was probably defective.

From these experiments it is evident that lead has quite a facility for forming double compounds with the halogens and analogous radicals, forming probably in many cases a series of such salts with various ratios between the halogens, all being quite stable and crystallising nicely.

SOME NEW SALTS OF CAMPHORIC ACID.

Although this acid has been known for over one hundred years, comparatively few of its salts have been prepared and studied. The present work was undertaken with a view of extending this list. The camphoric acid was prepared according to the directions of Wreden, by dissolving 150 grams of camphor in 2 litres of nitric acid, sp. gr. 1.27, and heating the solution 50 hours on the water-bath. The liquid was then saturated with sodium hydroxide, filtered, neutralised with hydrochloric acid, and the separated camphoric acid purified by crystallising from water. The yield was about the same as that obtained by Wreden, when great care was exercised in the purification by crystallising from water. The pure crystals gave the melting point 176° C. (uncorrected). A ten per cent. solution of caustic potash was saturated with camphoric acid, and solution of potassium camphorate so obtained was used in preparing the other compounds.

Manganese Camphorate (I. H. MANNING).—When a few drops of potassium camphorate were added to a nearly saturated solution of manganese sulphate in a small watch-glass, no precipitate was formed until heated on the water-bath. A white precipitate was then gotten which was easily soluble in cold water. This could always be reprecipitated on heating. In preparing this salt on a larger scale the mixture of potassium camphorate and manganese sulphate was heated to precipitation and the precipitate well washed with hot water. The precipitate was then dried at 100° C. If exposed in a moist condition it turned brown. There was a slight discoloration even when dried rapidly. At 150° decomposition was very slight; at 200° it was marked. When some of the manganese camphorate was dissolved in water and evaporated over sulphuric acid, a crust of the salt was obtained, but no crystal.

Analysis. (Three different preparations were used):

I. 0.2790 gram of substance gave 0.0859 gram Mn_3O_4.

II. 0.4460 gram of substance gave 0.1330 gram Mn_3O_4.

III. 0.4375 gram of substance gave 0.1330 gram Mn_3O_4.

I and III were determined by precipitating as carbonate, II by ignition.

	Calculated for $MnC_{10}H_{14}O_4$.	Found.		
		I.	II.	III.
Mn	23.07	22.07	21.39	22.50

As it was very·difficult to wash away all of the potassium camphorate, the low results are probably due to the same as an impurity.

Chromium Camphorate (I. H. MANNING).—On adding potassium camphorate to a solution of chromium sulphate, a heavy precipitate of a bluish-green color is formed. This is not very soluble and can be thoroughly washed with cold water. It can be dried at 100° C., losing all water at this temperature. Before reaching 150° slow decomposition sets in.

Analysis :

I. 0.4280 gram of substance gave on ignition 0.0859 gram Cr_2O_3.

II. 1.6370 grams of substance gave on ignition 0.1340 gram Cr_2O_3.

	Calculated for $Cr_2(C_{10}H_{14}O_4)_3$.	Found. I.	II.
Cr	14.81	12.93	14.40

The sample in I was different from that in II, and evidently not so pure.

Ferric Camphorate (I. H. MANNING).—A strong solution of ferric chloride was precipitated with potassium camphorate; a bulky yellowish precipitate was formed, quite insoluble in water and hence easily washed. This gave on drying at 100° a buff yellow powder. An analysis of this powder gave the percentage of iron as 19.34. The calculated percentage for $Fe_2(C_{10}H_{14}O_4)_3$ is 15.86. This powder was then probably a subcamphorate. It was treated once more with a strong solution of ferric chloride and again thoroughly washed. Analysis of this gave $Fe = 18.84$ and 18.90 per cent.

Mercuric Camphorate (I. H. MANNING).—A white heavy precipitate is formed on adding potassium camphorate to a concentrated solution of mercuric chloride. This was washed thoroughly and dried at 100° C. It forms a heavy white powder.

Analysis :

I. 0.4400 gram of substance yielded 0.2150 gram Hg.

II. 0.3840 gram of substance yielded 0.1920 gram Hg.

	Calculated for $Hg.C_{10}H_{14}O_4$.	Found. I.	II.
Hg	50.25	48.86	50.00

Aluminium Camphorate (G. W. EDWARDS).—Pure aluminium hydroxide was prepared, and this was then boiled with camphoric

acid in excess, using only a little water. The resulting aluminium camphorate is white and quite insoluble. It was dried at 100° and analysed.

	Calculated for $Al_2(C_{10}H_{14}O_4)_3$.	Found. I.	II.
Al	8.33	8.16	8.24

Nickel Camphorate (G. W. EDWARDS).—Pure nickel hydroxide was prepared and dissolved in camphoric acid, using as little water as possible. On heating this solution on the water-bath a crust, whitish-green in color, settled out. This was dried between bibulous paper and analysed.

Analysis:

	Calculated for $Ni(C_{10}H_{15}O_4)_2$.	Found.
Ni	12.76	12.03

The liquid poured off from this crust stood some days over sulphuric acid. A further settling out of the crust mentioned above was noticed; then small green crystals began to form. The liquid was filtered away from the crust and once more placed in the desiccator. The crystals obtained were dried on bibulous paper and analysed. It was impossible, however, to separate them from the crust. The analysis gave 12.50 per cent. of Ni. Hence the compound was the same as above.

Strontium Camphorate (G. W. EDWARDS).—Strontium carbonate is but slightly attacked by camphoric acid in the cold. On heating with water the evolution of carbon dioxide is rapid. The resulting strontium camphorate is soluble in water. Clusters of crystals are easily gotten on evaporation over sulphuric acid. The first analysis of the crystals was lost. Analysis of a crystalline crust resulted as follows:

	Calculated for $SrC_{10}H_{14}O_4.6H_2O$.	Found.
Sr	22.23	21.50
H_2O	27.45	27.75

DECOMPOSITION OF POTASSIUM CYANIDE.

By I. H. MANNING.

Under the head of "Condensation der Blausäure," v. der Pfordten discusses[1] the discoloration produced in solutions of potassium cyanide by the addition of free acids or of certain

[1] Ber. d. chem. Ges. **18**, 1875.

salts, or by the simple heating of the cyanide alone. This phenomenon was examined and studied to some extent by Mr. Wilkes[1] in this laboratory. Herr v. der Pfordten speaks of the decomposition of the cyanide, on heating some hours in a test tube placed in a water-bath, as being due "probably to the long continued action of the carbon dioxide of the air." That this could not be the case was shown by Wilkes, who proved that the decomposition took place in the cold with all carbon dioxide carefully excluded. The following experiments were undertaken to test the conclusion of Mr. Wilkes:

1st. A saturated or nearly saturated solution of pure potassium cyanide was placed in a tube, which was then sealed. Only a very minute amount of carbon dioxide could have been present, yet the usual changes of color indicating the decomposition were observed, and after some weeks the liquid had become black and a blackish deposit had formed.

2d. A similarly prepared tube, sealed, was placed in boiling water. Within five minutes a change to brownish-red was noticed and the color rapidly darkened.

3d. A similarly prepared tube was fitted with cork and tubes, and while it was in boiling water, carbon dioxide was passed over the surface of the liquid. The changes were very much as in experiment 2d. Apparently they were slightly delayed rather than hastened.

4th. Into a tube prepared as in 3d, hydrogen was passed in a rapid, continuous stream. The changes were decidedly delayed, and no very deep discoloration was obtained.

5th. If experiment 3d is reversed so that the carbon dioxide is passed above a cold solution of the cyanide, giving opportunity for its absorption, the change of color is of course rapid and deep.

From these experiments the conclusion can be drawn, that though carbon dioxide hastens the decomposition of the cyanide, as any free acid would do, yet it is not essential that it should be present, and in many cases the decomposition cannot be attributed to it, as is done by v. der Pfordten. It would seem that the decomposition was spontaneous, or, at most, assisted by the presence of traces of organic matter.

[1] Chemical News **51**, 45.

ON THE BROMINATION OF HEPTANE.

By F. P. Venable.

Schorlemmer has shown that the heptane from *Pinus sabiniana* is probably identical with that from petroleum and is a normal heptane. With regard to the action of the halogens upon this heptane he says:[1] " By the action of chlorine upon a normal paraffin not all the chlorides indicated by theory are formed, but only the primary and a secondary chloride which contains the group $CHCl.CH_3$; by the action of bromine upon normal paraffins from petroleum only secondary bromides corresponding to chlorides are formed."

In my inaugural dissertation (Göttingen, 1881, p. 14) I stated that I found other products formed during the bromination of normal heptane besides the secondary bromide, but did not examine them more closely. It seemed to me worthy of note at the time that when the unfractionated residue boiling above 170° C. (the secondary bromide boils at 165°–167°) was allowed to stand some time and was then distilled, it yielded, under evolution of hydrogen bromide, a fair proportion of secondary bromide boiling at 165°–167°. Time and material have both been lacking to me since the period of that research, and hence I have made no closer examination of this point.

As it would be a strange and not very easily accounted for fact if bromine yielded only secondary products acting on normal paraffins, I determined to make use of a recent opportunity to examine this action more closely.

It may be stated that in several brominations of this heptane made in recent years I have found the yield of secondary bromide to be only about 25 or 30 per cent. of the theoretical, much of the heptane remaining unattacked and much having to be rejected as boiling too high. The amounts of heptane brominated at one time varied from 100 to 300 grams, and the bromine usually dropped in as fast as it could be absorbed by the hot heptane. No quantitative data were preserved of these experiments, however. The yield is seriously unsatisfactory with so expensive a material as the heptane.

The following experiments were quantitative and conducted with especial care :

[1] This Journal 6, 31.

I. 100 *grams of pure heptane and* 160 *grams of bromine.*— The heptane was kept boiling gently over a naked flame. The flask containing it was provided with an inverted condenser and a dropping funnel for the bromine. The bromine dropped in the liquid, keeping it orange-red in color. The operation required five hours. The heavy oil was then washed with dilute sodium carbonate, then with water, and finally dried over calcium chloride. It was yellow with an orange tint. It was fractionated twice under a diminished pressure of 18–20 inches of mercury; then four times fractionated under ordinary pressure. The divisions were as follows:

Fraction I, 100°–120°, nearly all under 110°,   30 grams;
         II, 120°–162°,   5
         III, 162°–168°, mainly 164°–167°,   55
         IV, 168°–173°,   2
         V, 173°–183°, mainly between 176°–180°,   8
         VI, 183°–210°,   10

Probably one fourth, in bulk, of the oil was left partly charred in the fractionating flasks.

II. 100 *grams of pure heptane and* 160 *grams of bromine.*— The same apparatus as above was used, only the dropping funnel was drawn out to a capillary and about half an inch of this was submerged under the heptane. The bromine entered thus slowly and in the form of vapor. The heptane was at first at a lower temperature than in the first experiment. The temperature had to be increased later on, but so far as possible all excess over that necessary for the absorption of the bromine was avoided. The time consumed by the reaction was about thirteen hours. The oil was then treated as above. It was redder in color. It was fractionated as above, only one time less under ordinary pressure.

Fraction I, 100°–120°, mainly under 110°, 35 grams;
         II, 120°–162°,   5
         III, 162°–168°, mainly 164°–167°, 25
         IV, 168°–173°,   6
         V, 173°–183°, mainly 176°–180°,   20

No higher fraction than V was taken, though several grams could have been gotten by carrying the residue on to partial charring. Fraction V was in this case much more stable than the correspond-

ing fraction in the first experiment. It did not turn brown so quickly, nor deposit black spots on the glass.

III. 50 *grams of pure heptane and* 80 *grams of bromine.*—No heat was used in this case. The heptane was in a small open Erlenmeyer flask which was set in a vessel of water. . The bromine was poured in in small amounts and shaken until dissolved in the heptane, giving it a deep red color. Then it was allowed to stand in the light until only a yellow color remained. The temperature averaged about 6° C. The duration of the experiment was twenty-five days. The resulting oil was washed as above. It was bright yellow in color. It was fractionated once under diminished pressure and once under ordinary pressure. The following fractions were obtained :

Fraction I, 100°–120°, mainly under 110°, 12 grams ;
      II, 120°–162°,   2
      III, 162°–173°, mainly 164°–167°,   4
      IV, 173°–183°,   7
      V, 183°–195°,   very little ;
      VI, 195°–205°,   7 grams ;
      VII, 205°–215°,   12
      VIII, 215°–230°,   8

These fractions above 195° were heavy, of a brownish yellow color, and not showing much decomposition on standing. This third method of bromination was tried several times with similar results. Analyses of two proportions of the fraction coming over about 210° gave 56.4 per cent. and 58.0 per cent. of bromine ; $C_7H_{15}Br$ contains 44.69 and $C_7H_{14}Br_2$ 62.02 per cent. of bromine.

The results may be summed up thus : If we take into consideration the boiling points of the primary bromide (178.5°), secondary bromide, 164°–167°, and dibromide or heptylene bromide, 209°–211°, it will be seen that no mode of bromination tried yielded the secondary bromide alone. The first yields principally the secondary ; the second yields secondary and primary, whereas the third yields mainly compounds having a high percentage of bromine, probably several isomeric bromides of heptylene. The action of bromine then seems to be quite similar to that of chlorine.

REVIEWS AND REPORTS.

In a late number of this Journal (**9**, 458) there appeared a
report on " Recent advances in the chemistry of manganese,"
based upon the researches of Christensen and Franke.   Since
then another communication on this subject has come to hand, in
which Franke describes certain new double salts of manganese
with the alkaline sulphates, and discusses the structure of new
oxides which he has obtained from these salts by very simple
transformations.

The double salts, which serve as the starting points in this inves-
tigation, are all obtained from potassium permanganate and sul-
phuric acid.   As to whether one or another of these double salts
is obtained depends entirely on the concentration of the sulphuric
acid, the temperature, and the amount of permanganate used.
The space allotted to these reports will not permit the giving of
all the details involved in their preparation, and the reader is
referred to the original article.[1]

When potassium permanganate is added to concentrated sul-
phuric acid, a double salt of manganese and potassium having this
composition, $2Mn_2(SO_4)_3 + 5K_2SO_4$, separates. This compound is
obtained as a beautifully crystallised bordeaux-red salt, which
dissolves in dilute sulphuric acid with a brown color, in con-
centrated sulphuric acid with a violet color.   When heated
sufficiently it decomposes into manganese sulphate, sulphur
dioxide, and oxygen.   When treated with a considerable quantity
of water it is decomposed into manganese and potassium sulphates,
the hydrate of manganese dioxide, and sulphuric acid, a decompo-
sition which may be represented by this equation :

$$2Mn_2(SO_4)_3.5K_2SO_4 + 12H_2O = 6MnO_2 \text{ (hydrate)}$$
$$+ 5K_2SO_4 + 4MnSO_4 + 12H_2SO_4.$$
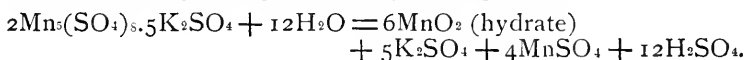
Manganous manganate, Mn_5O_8 or $3MnO_2.2MnO$.—When the
double salt $2Mn_2(SO_4)_3.5K_2SO_4$ is first added to water, a com-
pound which crystallises in glittering yellow leaflets separates.
This compound, if allowed to stand in the acid liquid, soon changes
to manganese sulphate and the hydrate of manganese dioxide.
By rapid filtration, however, and washing with water, it is possible
to obtain it in pure condition, and it is found to have the compo-
sition Mn_5O_8.   When this oxide is treated with dilute sulphuric
acid it breaks down, yielding manganous sulphate and manganese
dioxide ; and it is found further that the quantity of manganese
which exists in the solution as the sulphate is to the manganese which

[1] J. prakt. Chem. **36**, 168 and 451.

separates out as the hydrate of manganese dioxide, as $2:3$. This indicates that in the compound Mn_5O_8 the manganese exhibits two different valences towards oxygen, or, in other words, that we have two kinds of manganese in the compound, and the following structural formula is the simplest expression of these facts:

$$\overset{II}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{II}{Mn} \text{ or } 3\overset{}{MnO_2}.\,2MnO.$$
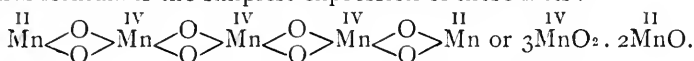
The compound Mn_5O_8 may be regarded as the manganous salt of a manganic acid of this formula,

$$\overset{}{^{HO}_{HO}}\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^{OH}_{OH},$$
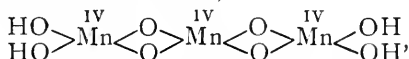
and all of the transformations of the double salt, $2Mn_5(SO_4)_8.5K_2SO_4$, can readily be explained by the aid of these formulas.

If we leave out of the equations the potassium sulphate, which after it is once split off takes no further part in the reaction, we have the decomposition of the compound, $2Mn_5(SO_4)_8.5K_2SO_4$, expressed by the following equations:

I. $Mn_5(SO_4)_8 + 4H_2O$

$$= \overset{II}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{II}{Mn} + 8H_2SO_4.$$

II. $Mn_5O_8 + 2H_2SO_4$

$$= 2\overset{II}{Mn}SO_4 + {^{HO}_{HO}}\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^{OH}_{OH}.$$

III. $3\overset{IV}{MnO_2}.\,2H_2O + 2H_2SO_4 = 4H_2O + SO_4$

$$= \overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn} = SO_4.$$

IV. $SO_4 = \overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn} = SO_4$

$$= (MnO_2) = SO_4 + O = Mn = O + MnSO_4.$$
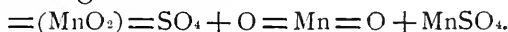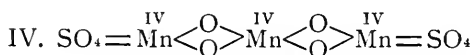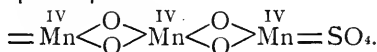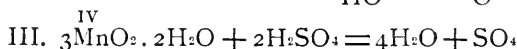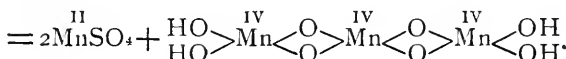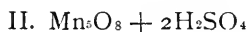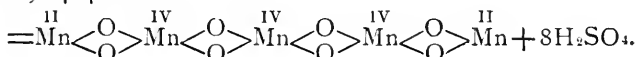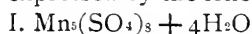
Now, just as we have an oxide, Mn_5O_3, which may be regarded as a manganous salt of a manganic acid, so we have still lower oxides in which this same relation exists. Thus the next lower member of this series would be an oxide of the formula Mn_4O_6, whose structure we may represent in this way:

$$\overset{II}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{II}{Mn}.$$
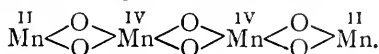
This we may consider as derived from an acid,

$$\overset{}{^{HO}_{HO}}\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!^{OH}_{OH}.$$
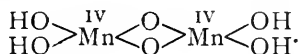
In the same way we may have an oxide Mn_2O_3 or

$$\overset{II}{Mn}\!\!<\!\!^O_O\!\!>\!\!\overset{IV}{Mn} = O,$$
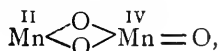
which may be considered the manganous salt of the acid,

$$\begin{matrix} HO \\ HO \end{matrix}\!\!>\!\!\overset{IV}{Mn} = O.$$
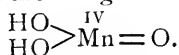
Of course, another view may be taken of an oxide of the composition Mn_2O_3, and we may regard it as a sesqui-compound in which the valence of the two manganese atoms is the same; such an oxide would have this formula: $O\!\!<\!\!\begin{matrix} \overset{III}{Mn} = O \\ Mn = O \end{matrix}.$

Franke has been able to obtain several of the compounds mentioned, but in no case has he been able to obtain compounds in which the valence of all the manganese atoms is the same, and he concludes that the existence of sesqui-compounds of manganese is highly improbable, if not impossible. Franke finds that when potassium permanganate is treated with sulphuric acid under slightly varying conditions, it is possible to obtain salts of the following compositions: $Mn_2(SO_4)_3.H_2SO_4 + 4H_2O$, $Mn_2(SO_4)_3.K_2SO_4$, and $Mn_2(SO_4)_3$. When these salts are decomposed by means of water they all yield, as the chief products of the decomposition, manganese sulphate, $MnSO_4$, and the hydrate of manganese dioxide, $MnO_2.H_2O$; and in every case the quantity of the manganese which exists in the solutions as the sulphate is to that precipitated as $MnO_2.H_2O$, as $1 : 1$, nearly.

This indicates that in these compounds, as in the compound $2Mn_5(SO_4)_8.5K_2SO_4$, we have two kinds of manganese; and the decompositions which these substances undergo can be best explained by these equations:

I. $\overset{II}{Mn}\!\!<\!\!\begin{matrix} SO_4 \\ SO_4 \end{matrix}\!\!>\!\!\overset{IV}{Mn} = SO_4 + 4H_2O$
$$= \overset{II}{Mn}\!\!<\!\!\begin{matrix} O \\ O \end{matrix}\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!\begin{matrix} OH \\ OH \end{matrix} + 3H_2SO_4;$$

II. $\overset{II}{Mn}\!\!<\!\!\begin{matrix} O \\ O \end{matrix}\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!\begin{matrix} OH \\ OH \end{matrix} + H_2SO_4$
$$= \overset{II}{MnSO_4} + \begin{matrix} HO \\ HO \end{matrix}\!\!>\!\!\overset{IV}{Mn} = O + H_2O.$$
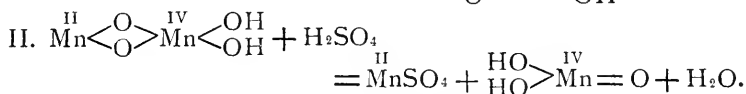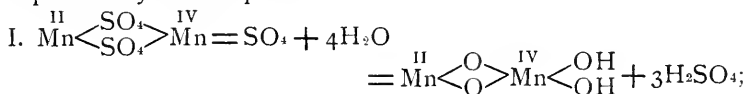
That the compound $\overset{II}{Mn}\!\!<\!\!\begin{matrix} O \\ O \end{matrix}\!\!>\!\!\overset{IV}{Mn}\!\!<\!\!\begin{matrix} OH \\ OH \end{matrix}$ is formed in the first stage of the above reaction is further shown by the fact that it is precipitated as such when the salt, $\overset{II}{Mn}\!\!<\!\!\begin{matrix} SO_4 \\ SO_4 \end{matrix}\!\!>\!\!\overset{IV}{Mn} = SO_4$, is treated with a dilute solution of sodium carbonate.

From these reactions there can be scarcely any doubt that the compound, $Mn_2(SO_4)_3$, has the structure represented by the formula $\overset{II}{Mn}\!\!<\!\!\begin{matrix} SO_4 \\ SO_4 \end{matrix}\!\!>\!\!\overset{IV}{Mn} = SO_4$, and further, since the compound, Mn_2Cl_6, shows similar properties and exhibits essentially the same decompositions, we cannot but assign to it a similar structure, viz. this, $\overset{II}{Mn}\!\!<\!\!\begin{matrix} (Cl_2) \\ (Cl_2) \end{matrix}\!\!>\!\!\overset{IV}{MnCl_2}$, in which two double chlorine atoms act as a bivalent element or radical.

On the action of concentrated hydrochloric acid on manganese dioxide.—The action of strong hydrochloric acid on manganese dioxide has also been carefully studied by Franke, and in the light of the results obtained the old view of the formation of chlorine by this reaction is no longer tenable, and the changes which take place and which lead to its formation can best be represented by the following equations :

I. $O = \overset{IV}{Mn} = O + 6HCl = \overset{H-(Cl_2)}{\underset{H-(Cl_2)}{}} > \overset{IV}{Mn} = Cl_2 + 2H_2O$;

II. $\overset{H-(Cl_2)}{\underset{H-(Cl_2)}{}} > \overset{IV}{Mn} = Cl_2 = 2Cl + MnCl_2 + 2HCl$;

III. $MnCl_2 + \overset{H-(Cl_2)}{\underset{H-(Cl_2)}{}} > \overset{IV}{Mn}.Cl_2 = \overset{II}{Mn} < \overset{(Cl_2)}{\underset{(Cl_2)}{}} > \overset{IV}{Mn} = Cl_2 + 2HCl$;

IV. $\overset{II}{Mn} < \overset{(Cl_2)}{\underset{(Cl_2)}{}} > \overset{IV}{Mn}.Cl_2 + 4H_2O = \overset{II}{Mn} < \overset{O}{\underset{O}{}} > \overset{IV}{Mn} < \overset{OH}{\underset{OH}{}} + 6HCl$;

V. $\overset{II}{Mn} < \overset{O}{\underset{O}{}} > \overset{IV}{Mn} < \overset{OH}{\underset{OH}{}} + 8HCl = MnCl_2 + \overset{H-(Cl_2)}{\underset{H-(Cl_2)}{}} > \overset{IV}{Mn} = Cl_2$
$+ 4H_2O.$
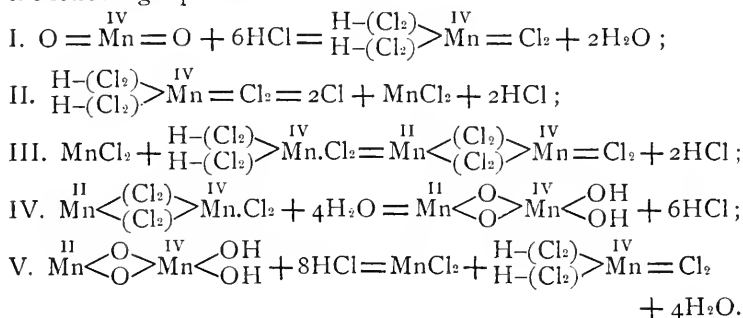
This reaction would go on repeating itself until at the end we should have left a strongly acid solution of manganous chloride, $MnCl_2$.   J. H. K.

THE UNION OF BODIES BY PRESSURE.

In former numbers of this Journal[1] attention has been called to the experiments of W. Spring and others upon the chemical reactions which take place between solid bodies under pressure. In the experiments described, Spring apparently succeeds in showing that solid bodies, finely pulverised and thoroughly mixed, unite chemically under pressure and produce a new compound, the amount of which is dependent upon the perfection and duration of contact of the original substances and the intimacy of their mixture.

The continuation of these experiments by the same investigator has yielded results which are of considerable interest. In his earlier work Spring[2] made use of simple substances ; in his later work compound substances are used. Mixtures of dry pure precipitated barium sulphate and sodium carbonate were subjected to the influence of a pressure of six thousand atmospheres under various conditions of temperature and duration of contact. In each experiment about one gram of a mixture, composed of one part of barium sulphate and three parts of sodium carbonate, was used. The product obtained as a result of the pressure was

[1] **6**, 129 and 212.   [2] Bull. Soc. chim. (Paris), 1885, **44**, 166.

thoroughly washed and the amount of barium carbonate in the insoluble residue was determined.

As in the case of the formation of sulphides and arsenides,[1] it was found that the percentage of barium carbonate produced by the action of sodium carbonate on barium sulphate under pressure, increases with the increase in the number of times the mixture is compressed. After a single compression the amount of barium carbonate produced was about one per cent. If the solid block produced by this compression is ground into fine bits and again subjected to the same pressure, and the process repeated a second time, about five per cent. of barium carbonate results. A sixth compression yielded nine per cent. of the product. These experiments show clearly the effect of a renewal of the faces of contact of two bodies capable of reacting under pressure. If the little blocks obtained by one, three and six compressions are left to themselves for some days and are then examined, it is found that, up to a certain limit, reached in about fourteen days, the amount of barium carbonate formed increases with the length of time during which the blocks have existed. The percentages found by Spring are:

Block produced at	o days.	7 days.	14 days.	21 days.	28 days.
First compression,	.94	1.60	3.08	3.94	3.84
Third "	4.78	6.78	9.01	...	9.15
Sixth "	8.99	9.94	10.89	...	11.08

This result, Spring thinks, is difficult to explain, unless we attribute to matter the power of diffusion, even when in the solid state.

The effect of heat is next examined, and, contrary to expectation, it is found that those blocks which, when allowed to remain for fourteen days at ordinary temperatures, contained 9.01 and 10.89 per cent. respectively, after being heated three hours at 120° contain only 7.07 and 9.89 per cent. of barium carbonate. Hence we are justified in concluding that heat is not the direct cause of the reactions set up in these mixtures.[2]

Spring[3] next reverses the reactions. He mixes three parts of dry sodium sulphate with one part of barium carbonate, and subjects this mixture to a pressure of six thousand atmospheres as before. When subjected to a single compression, 59.16 per cent. of the barium carbonate passed over into the sulphate. Three compressions yielded 69.25 per cent. of the sulphate, and six give 73.31 per cent. As the mere shaking of a mixture of the two salts in the proportions used produced 49.79 per cent. of barium sulphate, the difference between this figure and those given above will represent the effect upon it of one, three and six successive compressions. The length of time during which the two substances are allowed to remain in contact exerts quite as marked

[1] Cf. this Journal **6**, 213.   [2] Cf. this Journal **6**, 132.   [3] Bull. Soc. chim. (Paris), 1886, **46**, 299.

an influence upon the amount of the new product formed as was noted in the former case. Here, too, there appears to be a limit beyond which the reaction refuses to proceed. The results obtained in this series are as follows:

Block produced at	o days.	7 days.	14 days.
One compression,	59.16	63.91	64.66
Three compressions,	69.25	74.98	77.38
Six compressions,	73.31	80.68	80.31

When the little block produced by one compression is kept at a temperature of 160° for six hours, it is found to contain only 34.66 per cent. of barium sulphate instead of 59.16 per cent. The block produced by six compressions now contains only 46.38 per cent. instead of 73.31 per cent. These results substantiate those obtained in the first series, and show plainly that the reactions which have taken place cannot be due to a rise in temperature during the process of compression.

From a consideration of these two sets of experiments Spring regards as fairly well established the facts that—

1. Diffusion may take place as well in solid bodies as in those which are fluid.

2. Matter assumes under pressure a condition relative to the volume it is obliged to occupy.

3. For the solid state, as for the gaseous, there is a critical temperature, above or below which changes by simple pressure are no longer possible.

Liquid bodies, then, become solidified if their specific volumes are smaller in the solid than in the liquid state, and conversely, provided that in each case the critical temperature is taken into account. These results of Spring's are accepted by most chemists as worthy of very careful consideration. Mr. Hallock,[1] however, has recently criticised both the experiments and the conclusions of the French chemist, but as he seems to have misunderstood[2] Spring's position, and even his very language, a great deal of weight will not be attached to his criticism.   W. S. B.

GERMANIUM.

The scarcity of the material in which this element occurs has prevented a very active study of its properties and compounds; nevertheless, certain recent advances have been made along this line, and these are deserving of careful notice.[3] Winkler's latest experiments have had to do especially with the compounds of germanium with monatomic elements or radicals, such as the halogens, the alcohol

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[1] Am. J. Sci. **34** (1887), 277.   [2] Ibid. **35** (1885), 78, and Bull. Soc. chim. (Paris), **48**, 630.
[3] J. prakt. Chem. **36**, 177.

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radicals, and hydrogen. As the author says,[1] "These experiments are still incomplete; nevertheless they may serve as the starting points for further investigation, and even in their present state throw a good deal of light on the chemical character of germanium."

Germanium dichloride, $GeCl_2$.—This compound has not as yet been obtained in pure condition. Attempts to make it by passing hydrochloric acid gas over heated germanium have resulted in the formation, not of the dichloride, but of germanium chloroform, $GeHCl_3$.

Germanium tetrachloride, $GeCl_4$.—This compound can best be prepared by gently heating a mixture of germanium sulphide and mercuric chloride. The resulting fluid remains liquid at a very low temperature and does not solidify at $-100°$.

Germanium chloroform, $GeHCl_3$.—This compound is prepared by passing dry hydrochloric acid gas over heated germanium. It is a colorless liquid which quickly becomes milky on exposure to air and also when distilled. This change is probably due to oxidation which results in the formation of an oxychloride, $GeOCl_2$.

Germanium oxychloride, $GeOCl_2$ (?).—This compound is probably formed by oxidation of germanium chloroform. As yet it has never been obtained in a condition sufficiently pure for analysis.

Germanium tetrabromide, $GeBr_4$.—When gently heated, germanium burns in bromine vapor with a pale yellow flame. The compound thus formed is the tetrabromide. It can be best prepared by heating together powdered germanium and mercuric bromide. In this way it is obtained as a clear, limpid, strongly fuming liquid which at $0°$ solidifies to a white crystalline mass.

Germanium difluoride, GeF_2.—This compound has not been isolated as yet, though there are some facts which speak for its existence.

Germanium tetrafluoride, GeF_4.—This compound is formed by treating germanium oxide with hydrofluoric acid. It crystallises from its thick, syrupy solution in white wart-like crystals which are very deliquescent. This conduct is similar to that of titanium fluoride, with this exception, that titanium fluoride and also zirconium fluoride give insoluble oxyfluorides when dissolved in cold water, whereas germanium fluoride forms a clear solution. Germanium fluoride is found to have the composition represented by the formula $GeF_4.3H_2O$. When heated with water it passes over partly into an oxyfluoride, and when the salt is heated to the boiling point of sulphuric acid it is partially decomposed into hydrofluoric acid and germanium oxide, but a portion of the compound passes off unchanged in the form of vapor.

Hydrofluogermanic acid, H_2GeF_6.—This compound is made by conducting the vapors of germanium fluoride, GeF_4, into water. In this way a clear liquid is obtained having a strong acid reaction. On allowing this liquid to evaporate spontaneously a thick acid

liquid is obtained, from which small crystals of germanium oxide separate. Caustic potash and potassium salts cause a rich precipitation of the double fluoride of germanium and potassium from the acid liquid.

Potassium-germanium fluoride, K_2GeF_6.—This salt can easily be prepared by adding a concentrated solution of potassium chloride to a solution of germanium oxide in hydrofluoric acid. It is found to crystallise in the hexagonal system and, according to Krüss and Nilson,[1] it is isomorphous with the ammonium-silicium fluoride, $(NH_4)_2SiF_6$. Like the corresponding silicium compound it is found to be anhydrous, while the double fluorides of titanium, zirconium, and tin contain one molecule of water of crystallisation.

Compounds of germanium with alcohol radicals.—In his paper on the periodic law Mendelejeff,[2] predicting the properties of eka-silicium, says that " a slight difference between eka-silicium and titanium will consist in the fact that this element, like silicium and tin, will be able to form volatile metallo-organic compounds, whereas titanium can form no such compounds ; and further, judging from the properties of silicium and tin, the ethyl compound of eka-silicium will boil at 160° and have a density of about 0.96." This prognostication has been verified in a remarkable way, and there can be no doubt that this hypothetical eka-silicium of Mendelejeff and germanium are the same element.

Germanium ethyl, $Ge(C_2H_5)_4$.—This compound is obtained by treating germanium tetrachloride with zinc ethyl. It is a colorless liquid of a weak leek-like odor ; its specific gravity is slightly less than that of water, and it boils at 160°. At ordinary temperatures it is not acted on by the oxygen of the air; it is easily ignited, however, and burns with a dark yellowish-red flame. Its vapor forms explosive mixture, with oxygen.

Germanium ultramarine (?).—When germanium oxide is fused with soda and sulphur in a porcelain crucible, a small quantity of a blue compound is formed which is believed to be a germanium ultramarine. Attempts to prepare this in quantity have, however, resulted in failure.   J. H. K.

NOTE.

The Determination of Morphine in Opium.

The Austrian Pharmaceutical Society recently offered the following as a prize question :

A comparative examination of the best known methods for the determination of the quantity of morphine in opium, and, if pos-

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[1] Ber. **20**, 1699.   [2] Ann. Chem. (Liebig) Suppl. **8**, 200.

sible, the perfecting of a new and very simple method sufficiently accurate to meet the practical need.

The satisfactory treatment of this subject secured the prize to A. Kremel, whose paper is given below in abstract. Five grams of the opium powder are macerated in a small flask, with 75 cc. of lime water, for 12 hours, with frequent shaking ; this is then filtered through a plaited filter. (The ratio 1 part of opium to 15 parts officinal lime water has been arrived at by practice, and in this way there is obtained a nearly neutral or slightly acid filtrate. Should the liquid after the maceration react alkaline, then less lime water should be used.) To 60 cc. of the filtrate, corresponding to 4 grams of opium, which is brought into a weighed flask of such a size as to be nearly filled by the ether and ammonia, there is added 15 cc. of ether and 4 cc. of normal ammonia. The flask is then well corked and the contents mixed by gentle agitation. The flask is then set aside for 6 to 8 hours, the temperature being kept at 10°–15°. At the end of that time the ethereal layer is removed, 5 cc. of fresh ether added, and the flask gently shaken ; the ether is again removed, and finally the crystals of morphine, which have separated out, are collected on a small plaited filter. The crystals which remain in the flask are washed with 5 cc. of distilled water ; this wash-water is brought on the filter, and finally the flask and also the filter and its contents are dried at 100°. The crystals on the filter are transferred to the flask, and this is then dried until a constant weight is obtained. The morphine thus obtained is perfectly pure, and dissolves *completely*, though slowly, in 100 parts of saturated lime water.

The mode of procedure is the same for opium extract, 1 part of extract is treated with 20 parts of lime water. Opium tincture is first mixed with powdered glass which has been washed with hydrochloric acid, and the mixture evaporated to dryness on the water-bath ; the residue is then treated with a quantity of lime water equal to the quantity of tincture used in the experiment.— (*Pharm. Post.* 1887, **20,** 661 ; *Abstract in Chemisch. Repert. of the Chemiker Zeitung,* 1887, 258.)

AMERICAN

CHEMICAL JOURNAL.

ON THE COMBUSTION OF WEIGHED QUANTITIES OF HYDROGEN, AND THE ATOMIC WEIGHT OF OXYGEN.

By E. H. Keiser.

The atomic weight of oxygen is the foundation upon which the entire system of atomic weights rests. It is unquestionably one of the most important constants in chemical science. At the present time the opinions of chemists differ as to its most probable value. While many accept 15.96 as the mean result of all the more trustworthy determinations, others are inclined to believe that the whole number 16 approaches nearer to the truth. Both numbers lie between the maximum and minimum values that have been obtained by the best methods heretofore employed in determining this constant. As all the other atomic weights, with few exceptions, depend upon that of oxygen, it follows that two values may be obtained for each element accordingly as one or the other of these numbers is made the basis of the calculation. As a result of this, all the atomic weights are uncertain to the extent of about one quarter per cent. of their values. It is very desirable for this reason, as well as for others of a more speculative nature—as, for example, the question of the validity of Prout's hypothesis—that the atomic weight of oxygen should be redetermined with the very greatest care.

In a preliminary paper[1] I called attention to a new method of determining this atomic weight, by means of which, it seemed to

[1] Ber. d. chem. Ges. **20**, 2323.

18

me, more accurate results could be obtained than by the older methods. Briefly stated, it consists in burning weighed quantities of hydrogen by passing the gas over heated copper oxide, and weighing the water formed. From the weight of water obtained by the combustion of a known weight of hydrogen, the atomic weight of oxygen may be readily calculated.

It is evident that the accuracy of the results obtained by this method must depend to a large extent upon the purity of the hydrogen that is used, and upon the correctness with which it is weighed. It is, however, extremely difficult to weigh accurately any considerable quantity of hydrogen in the gaseous state. If Regnault's method of compensated glass globes be used, it would require very large and heavy vessels to weigh comparatively small quantities of hydrogen, and in weighing such large globes errors may arise from many different sources. Lord Rayleigh[1] has recently pointed out a source of error in this method which appears to have been overlooked by all who had previously used it. He has shown that the volume of a glass globe is larger when it is full than when it is empty, and that the weight of the gas contained in it is not equal to the difference in weight of the full and empty globe.

In order to be able to weigh hydrogen accurately, I have taken advantage of the beautiful discovery made by Thomas Graham in the year 1866. Metallic palladium, as he has shown, has the power at ordinary temperatures of occluding many hundred times its own volume of hydrogen gas. The palladium hydrogen which is thus formed is stable at ordinary temperatures, and the metal retains the hydrogen even in a vacuum. If, however, the temperature be raised above 100°, then the gas will be expelled in a slow and regular current. Under atmospheric pressure nearly all of the hydrogen can be driven out at temperatures below 200°. By enclosing a quantity of metallic palladium in a glass vessel from which the air has been removed, and saturating it with pure hydrogen, a large volume of the gas may be condensed into a small space. If now the temperature be raised gradually, the gas will be driven out slowly and regularly. If the vessel be weighed before and after the heating, the loss in weight will equal the weight of hydrogen that has been expelled. It is possible, therefore, with an apparatus of small dimensions to weigh comparatively

[1] Chem. News **57**, 73.

large volumes of hydrogen. Preliminary experiments showed that 100 grams of palladium foil will readily absorb from .6 to .7 gram of hydrogen, and that with an apparatus having a volume of about 150 cc. and weighing 130 grams, it is possible to weigh, with great accuracy, an amount of hydrogen which in the gaseous state would occupy a volume of from 7 to 8 litres. A glass globe that could hold the same quantity of gas would be much heavier than the tube containing the palladium ; and such a globe, owing to its much greater volume, could not be weighed with nearly the same degree of accuracy.

There is, however, another and no less important advantage gained in weighing hydrogen in the condition of palladium hydrogen. It is necessary that the hydrogen which is weighed and burnt for the purpose of determining the atomic weight of oxygen should be absolutely pure. The greatest difficulty connected with the preparation of pure hydrogen is to get rid of all traces of air. Other impurities may be avoided by starting with chemically pure materials for the preparation of the gas, and by using appropriate absorbing and drying reagents for purifying it. If air is present, the oxygen of the air may be removed by passing the gas over heated copper. Water will be formed, and this may be absorbed by means of phosphorus pentoxide. But there is no way of removing the nitrogen. Palladium, however, has not the power of absorbing nitrogen. If the hydrogen used for saturating the palladium contains nitrogen, the hydrogen will be occluded, the nitrogen will remain unacted upon ; and, after the palladium has been saturated, the nitrogen may be removed from the palladium tube by means of an air pump.

Thomas Graham,[1] who first studied the behavior of palladium toward gases, found that hydrogen was the only constituent of illuminating gas that possessed the power of penetrating palladium foil. Wöhler[2] has shown that palladium cannot absorb ethylene, and that at high temperatures it decomposes hydrocarbons into carbon and hydrogen. Wilm[3] has also observed that at high temperatures palladium can decompose hydrocarbons, and he has shown that the hydrogen is absorbed by the metal, while the carbon is left on its surface in an extremely finely divided condition. Hempel[4] has found that from a gas mixture containing hydrogen,

[1] Ann. Chem. (Liebig) Supp. Band 5, 61.
[2] Ann. Chem. (Liebig) 184, 129.
[3] Ber. d. chem. Ges. 14, 874.
[4] Ber. d. chem. Ges. 12, 636.

marsh gas, and nitrogen, the hydrogen may be completely absorbed and separated from the other constituents by means of metallic palladium.

Preliminary Experiments.

While it thus appears from a study of the literature of palladium that this metal has not the power of absorbing nitrogen or marsh gas, ethylene, and other hydrocarbons, it, nevertheless, seemed necessary to determine by careful preliminary experiments whether, under the conditions under which the palladium was to be used for occluding hydrogen, it might not be able to take up minute traces of nitrogen or oxygen. For this purpose several pieces of palladium foil, weighing together 140 grams, after being carefully cleaned and rolled into the shape of a cylinder, were placed in a wide glass tube which was closed at one end. The open end was drawn down to a small diameter and fused to a three-way glass stop-cock. The tube was exhausted with a Geissler air pump and the metal heated to a temperature of about 400° in the vacuum. The glass tube was protected from the flame by a wrought iron trough containing a layer of magnesia. After the metal had been heated for some minutes in the vacuum, the lamp was removed. Pure dry nitrogen gas was then admitted by means of the three-way stop-cock, and the metal was allowed to cool down slowly and to remain for several hours in an atmosphere of nitrogen. The tube was thereupon exhausted with the pump and, after a vacuum had been obtained, it was again heated. Not the minutest trace of gas was given off. If only a small fraction of a cubic centimeter of nitrogen had been driven out of the palladium it would have been detected because the pump was kept in constant operation. The experiment was repeated several times, but the result was always the same. In one experiment the palladium tube was exhausted and weighed. It was then heated in the vacuum and treated with nitrogen as above described. After being again exhausted the weight was found to be the same as before. It appears, therefore, that under these conditions palladium has not the power of absorbing nitrogen; but these are the conditions that were found to be the most favorable for the occlusion of hydrogen. After the metal had been heated in a vacuum it was allowed to cool in an atmosphere of hydrogen. The gas was absorbed in large quantities. When perfectly cold the tube was exhausted and

weighed. It was found to be nearly a gram heavier than it was before the hydrogen had been occluded. The hydrogen was held so firmly by the palladium that when the tube was exhausted with the air pump the palladium hydrogen showed but a very slight tension. On warming it, however, the gas was given off in large quantities. Other experiments made with oxygen showed that this gas also, under the conditions described above, is not absorbed by palladium.

Experiments were now made for the purpose of determining what the effect would be of treating palladium with hydrogen containing a small percentage of air. The metal was heated in a vacuum and then allowed to cool in an atmosphere of hydrogen containing air. The hydrogen was rapidly absorbed, but at the same time a minute quantity of moisture was deposited on the interior surface of the tube. When no more gas was absorbed the palladium tube was connected with a weighed phosphorus pentoxide U tube and heated. As the gas escaped from the palladium tube the film of moisture gradually disappeared. The U tube was weighed again after the hydrogen in it had been displaced by air. It was found to have increased in weight, thus showing that when palladium is treated with hydrogen containing air the oxygen is converted into water. The idea suggested itself that perhaps hydrogen dioxide might also be formed, and that the palladium hydrogen in the presence of nitrogen might cause the formation of ammonia. The palladium was therefore treated again with hydrogen containing air, and after the metal had been saturated the palladium tube was connected with a Geissler potash bulb containing Nessler's solution. The gas was thereupon driven out of the palladium tube by heating, and although more than six litres of hydrogen were passed through the Nessler's solution, not the faintest reaction for ammonia was obtained. The experiment was repeated, but in this case, instead of using Nessler's reagent, the gas from the palladium tube was led through a solution of potassium iodide and starch paste to which a small quantity of ferrous sulphate had been added. No reaction for hydrogen dioxide was obtained. Another experiment was made for the purpose of determining whether palladium itself is not volatilised when palladium hydrogen is decomposed. A quantity of palladium foil was carefully weighed and then saturated with hydrogen. The hydrogen was then completely removed by heating in the presence of air. On weighing the foil again its weight was found to be unchanged.

The conclusions drawn from the results of these preliminary experiments are as follows: Palladium at temperatures below 400° cannot occlude oxygen or nitrogen. If palladium be treated with hydrogen containing a trace of nitrogen, the hydrogen will be occluded, but the nitrogen will remain unabsorbed, and it may be removed from the vessel containing the palladium hydrogen by means of an air pump. If the tube containing the palladium hydrogen be heated pure hydrogen will be expelled, and the weight of the gas thus driven out may be determined from the loss in weight of the palladium tube. If palladium be treated with hydrogen containing traces of air, the hydrogen will be occluded, the nitrogen will remain unabsorbed, but the oxygen will be converted into water. By means of an air pump the nitrogen and a portion of the water may be removed from the tube containing the palladium. On heating the tube the hydrogen which is driven out will carry with it traces of moisture. The weight of the hydrogen and moisture thus expelled may be determined from the loss in weight of the palladium tube, and the amount of moisture present in the hydrogen may be determined by passing the gas through a weighed phosphorus pentoxide U tube. Lastly, palladium itself is not volatilised when palladium hydrogen is decomposed.

Apparatus for Preparing and Weighing the Hydrogen.

The construction of the palladium tube that was used for weighing the hydrogen in the atomic weight determinations is shown in Fig. 1. The expanded portion a contained 140 grams of palladium foil that had previously been thoroughly cleaned, and which, before being placed in the tube, had been heated to a bright red heat in a vacuum. The three-way glass stop-cock b was fused to a, and its construction will be readily understood from the cross-section drawing b'. The end c was ground to fit accurately into the phosphorus pentoxide tube d, shown in Fig. 3. The diameter of a was 3 cm. and its length 14 cm. The total length of the tube including the stop-cock was 26 cm.; its weight, including that of the palladium, was 204.5 grams. The first six determinations were made with a somewhat smaller tube which contained only 100 grams of palladium and weighed 160 grams.

The hydrogen that was used for saturating the metal was prepared by the action of pure dilute sulphuric acid upon chemically

Fig 3.

Combustion Furnace.

N →
O. or Air ←

Fig 2.

Combustion Furnace.
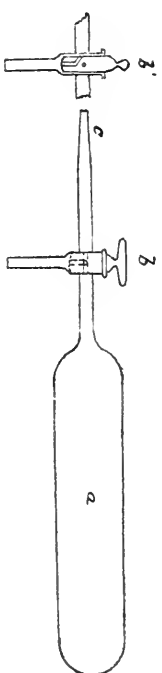
Fig 1.
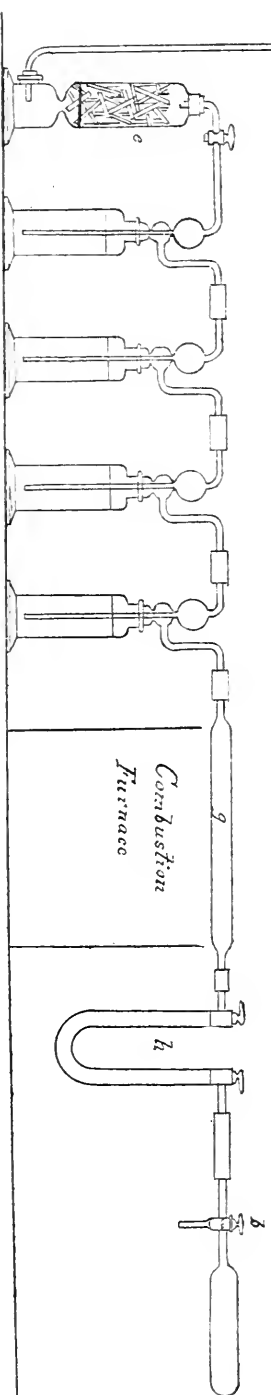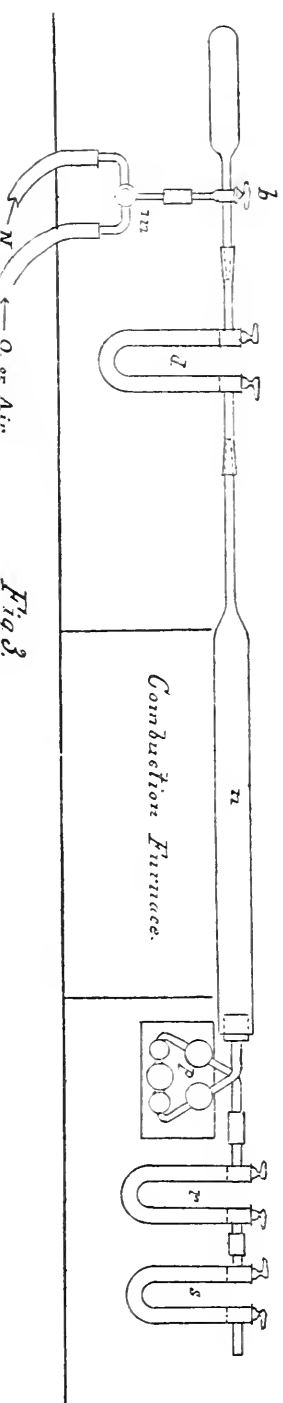
pure zinc, free from arsenic. The apparatus for generating and purifying the gas is shown in Fig. 2. The zinc was placed in e, and it was acted upon by the dilute sulphuric acid contained in f. The vessel f was supported by a shelf, and was connected with e by means of glass tubing as shown in the figure. After leaving the generating apparatus the hydrogen passed through four wash-bottles. The first one contained a solution of lead hydroxide in concentrated caustic potash; the second one, a concentrated solution of potassium permanganate acidulated with dilute sulphuric acid; the third one, an alkaline solution of potassium permanganate; and the fourth one, pure concentrated sulphuric acid. To the fourth wash-bottle was connected the combustion tube g, which contained metallic copper. The copper was obtained by the reduction of the chemically pure oxide in a current of hydrogen. A small gas furnace supported the combustion tube, and while the gas was being generated the tube was kept at a bright red heat. After having passed over the heated copper the gas was conducted through the U tube h, which was filled with phosphorus pentoxide. The joints of the apparatus were made of thick-walled rubber tubing; they were all wired securely and coated with varnish.

The method of charging the palladium with hydrogen was conducted as follows: The palladium tube, resting upon a trough of sheet iron and protected from contact with the iron by a layer of magnesia, was connected with a Geissler air pump and exhausted. After the palladium had been heated to a temperature of about 250° for fifteen minutes in the vacuum, the stop-cock b was closed, and, while the tube was still warm, the end c was connected with the U tube h as shown in Fig. 2. Meanwhile all the air in the hydrogen generating apparatus and the wash-bottles had been expelled, as the evolution of gas was begun more than one half hour before the palladium tube was attached. For several minutes more the hydrogen was allowed to escape from the downward branch of the stop-cock, to which a straight glass tube dipping in mercury was attached, to ensure that all the air had been displaced in the tube connecting the palladium vessel with the U tube h. The stop-cock was then turned carefully so as to allow a slow stream of hydrogen to enter the warm palladium tube. Under these circumstances the metal absorbs the hydrogen so rapidly that it is necessary to open the stop-cock very cautiously, otherwise the gas will pass too rapidly through the wash-bottles.

While the hydrogen is being absorbed the metal cools down very slowly, because considerable heat is evolved in the formation of palladium hydrogen. When the absorption of gas had become very slow—and from 2 to 2½ hours sufficed for saturating 140 grams of palladium—the stop-cock was closed and, after being again attached to the Geissler pump, the tube was exhausted. By this means nitrogen, if it should have been present in the hydrogen used for saturating the palladium, was removed. Palladium hydrogen gives off hydrogen very slowly in a vacuum, so that, if the pump be kept in operation for some time, all traces of nitrogen in the palladium tube and in the pump itself may be completely carried out by means of this slow evolution of gas. After the removal of the nitrogen the tube was closed and disconnected from the pump. It was then thoroughly cleaned and placed in the balance room.

A short beam analytical balance, made by Becker Brothers, New York, was used for all the weighings. It could carry safely 225 grams in each scale pan, and was adjusted so that a load of one milligram caused a deflection of 12 divisions of the ivory scale. All weighings were made by the method of vibrations. In weighing the palladium tube and the tubes used for condensing and absorbing the water, each tube was compensated by a similar one, of the same external volume, constructed of the same material, and having nearly the same weight. The weights were also made by Becker Brothers; the smaller ones were of platinum, the larger ones of brass. One of the 10 gram weights was selected as the standard, and the relative values of all the others were determined by the well known method of adjustment. All atomic weight determinations were made on days when the weather was clear and dry ; and, as a combustion including the weighings could be made in four hours, the barometer, temperature of balance-room, and the humidity of the air remained practically constant during each determination.

Method of Burning the Hydrogen.

The arrangement of the apparatus that was used for burning the hydrogen is shown in Fig. 3. The palladium tube was connected by means of a ground-glass joint with the weighed phosphorus pentoxide tube *d*. The latter tube served to determine the amount of moisture in the hydrogen that was expelled from the palladium tube. The tube *d* was connected by means of

another ground-glass joint with the combustion tube n, which contained copper oxide. For the purpose of obtaining pure copper oxide, the chemically pure granular oxide of commerce was reduced in a current of pure hydrogen, and the metallic copper thus obtained was heated to a bright red heat in a vacuum. All volatile matter having been removed in this way, the copper was oxidised with pure oxygen. In each determination the reduced copper was again oxidised to copper oxide, so that the condition of the combustion tube was the same at the beginning and end of the combustion. The copper oxide that was used in the determinations recorded below had been repeatedly reduced and oxidised in preliminary determinations. The combustion tube was 90 cm. in length and had an internal diameter of 15 mm. It was filled to within 10 cm. of the open end, and it contained so much copper oxide that there was never more than one half of it reduced in any determination. The object of this large excess was to insure the complete combustion of the hydrogen. The water formed by the combustion of the hydrogen was condensed in the bulb apparatus p and the U tube r. When not connected with the combustion tube, p was closed by means of ground-glass plugs. A tightly fitting rubber stopper was used to connect the bulb apparatus with the combustion tube. During the combustion the bulbs were kept cool by being surrounded with cold water placed in a glass dish. The U tubes r and s contained phosphorus pentoxide, and s served to protect r in case air should be drawn backward into the combustion tube. To the downward branch of the stop-cock of the palladium tube was attached the three-way glass stop-cock m, by means of which either oxygen or nitrogen could be passed through the apparatus. The oxygen before entering was conducted through concentrated sulphuric acid, concentrated caustic potash, and over phosphorus pentoxide. The nitrogen was purified by passing through concentrated sulphuric acid, concentrated caustic potash, over red-hot copper to remove the oxygen, and then over phosphorus pentoxide.

The combustion of the hydrogen was conducted in the following manner : In the first place, the copper oxide was heated to a bright red heat in a current of dry air so as to remove hygroscopic moisture. The U tube d, the palladium tube, and the tubes p and r, after having been carefully weighed, were connected as shown in Fig. 3. The tube s and the stop-cock m were then attached, and a stream of nitrogen was allowed to pass through

the apparatus for from 20 to 30 minutes to expel the air, thus avoiding the possibility of an explosion when the hydrogen was admitted. The palladium tube was thereupon warmed gently, and, after its temperature had risen to a little above 100°, the stop-cock *b* was turned slowly so as to cut off the current of nitrogen and to allow a slow stream of hydrogen to pass through *d* into the copper oxide tube. In warming the palladium tube the flame never came in contact with the glass. The tube was always supported by an iron trough, and the glass was protected from contact with the iron by a layer of magnesia. The rate at which the gas was expelled and burnt could be easily regulated by raising or lowering the temperature of the palladium tube. After the greater quantity of hydrogen had been burnt and the current of gas had become very slow, the stop-cock *b* was turned to its original position, thus closing the palladium vessel and readmitting the stream of nitrogen. The palladium tube was then allowed to cool ; in so doing the metal reabsorbs the gaseous hydrogen that is present in the tube, and at the end of the operation the pressure in the interior of the tube is the same as at the beginning. After the nitrogen had carried all of the hydrogen into the combustion tube, oxygen was admitted through *m*, and the reduced copper was converted into copper oxide. The oxygen was then displaced by a stream of dry air, and the copper oxide was allowed to cool.[1] The tubes were then disconnected and, after being cleaned, were taken to the balance room. They were allowed to stand a suffi-cient length of time to acquire the temperature of the room, and were then weighed.

The weight of water formed was determined from the increase in weight of *p* and *r*. To the weight of liquid water in *p* was added the weight of air which it displaced, thus its weight in vacuo was

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[1] For the purpose of determining whether traces of hydrogen could escape combustion by this method, the following experiment was made : About one half of the copper oxide in the combustion tube was reduced with hydrogen, then a current of carbon dioxide was allowed to enter at *m* so as to carry all of the hydrogen into the combustion tube. The gases after passing over the copper oxide were conducted through caustic potash, then over phosphorus pentoxide, and again over copper oxide contained in a second combustion tube. To this second combus-tion tube was attached a weighed phosphorus pentoxide tube. If any hydrogen should have escaped combustion in the first combustion tube, where it was diluted with a large excess of carbon dioxide, it must have accumulated in the caustic potash bulbs. Subsequently when air was drawn through the apparatus, the hydrogen would have been carried into the second com-bustion tube in much more concentrated condition than it left the first one. In this tube it would have been burnt, and the phosphorus pentoxide tube would have increased in weight. Although the experiment was tried several times, the weight of the latter tube always remained constant.

obtained. The weight of the tube d remained the same as at the beginning of the combustion, provided the hydrogen that had been used for saturating the palladium was free from oxygen. In this case the loss in weight of the palladium tube gave the weight of hydrogen that had been burnt. If, however, a small quantity of oxygen was present in the hydrogen used for charging the palladium, then the gas that was expelled from the tube contained a trace of moisture, and, in this case, the increase in weight of d had to be deducted from the apparent weight of hydrogen. In all carefully conducted atomic weight determinations the increase in weight of d was never found to be more than a fraction of a milligram.

Atomic Weight of Oxygen.

The following results have been obtained by this method :

No. of Experiment.	Wt. of H burnt.	Wt. of Water Obtained.	Atomic Wt. of Oxygen.
1	.34145 grams.	3.06338 grams.	15.943
2	.68394	6.14000	15.955
3	.65529	5.88200	15.952
4	.65295	5.86206	15.954
5	.66664	5.98116	15.944
6	.66647	5.98341	15.955
7	.57967	5.20493	15.958
8	.66254	5.94758	15.952
9	.87770	7.86775	15.950
10	.77215	6.93036	15.951
Total	6.55880	58.86263	[15.9492]

From these numbers the ratio of hydrogen to oxygen is found to be : $H : O :: 6.55880 : 52.30383$, or $H : O :: 1 : 7.9746$, and the atomic weight of oxygen $= 7.9746 \times 2 = 15.9492$. Maximum value 15.958 ; minimum value 15.943. The result obtained from these determinations appears, in the author's mind, to furnish very strong evidence in favor of the view that the relative atomic weight of oxygen cannot be greater than 15.96, and that its true value is probably a little less than this number.

Several months after the appearance of my preliminary paper, and while this investigation was still in progress, Prof. J. P. Cooke and Mr. T. W. Richards published the results of a redetermination of the atomic weight of oxygen by the same general method which

I had proposed. They also have determined the quantities of water formed by the combustion of weighed amounts of hydrogen. But our work differs very much in the methods employed for weighing the hydrogen. Messrs. Cooke and Richards have weighed it in the gaseous state, and have used Regnault's method of weighing gases by means of compensated glass globes. Aside from the difficulties of weighing accurately such large glass globes, owing to air currents, changes of atmospheric conditions, etc., and the fact that a comparatively heavy vessel must be used for weighing but a small quantity of hydrogen; this method is open to the objection that all impurities that may be present in the gas, such as traces of nitrogen or air, are weighed as hydrogen. Errors caused by impurities in the hydrogen tend to diminish the atomic weight of oxygen. On the other hand, Lord Rayleigh has pointed out another source of error which tends to increase the atomic weight. As mentioned above, the volume of a glass globe is not the same when it is full and when it is empty, and the difference between the full and empty weighings is less than the true weight of hydrogen.

The method which I have employed for obtaining weighed quantities of hydrogen seems to me to be free from these sources of error. By using palladium, a considerably larger quantity of hydrogen may be obtained from a very much smaller and lighter apparatus, consequently the gas can be weighed with greater accuracy. Impurities such as nitrogen and oxygen are eliminated, and as the pressure in the interior of the palladium tube is the same at the beginning and end of the determination, and as the vessel is of small dimensions, there can be no change of volume of the tube. Nevertheless the value for the atomic weight of oxygen obtained by Messrs. Cooke and Richards agrees very closely with that obtained by this method. Value obtained by Cooke and Richards $= 15.953$.[1] Value obtained by the palladium method $= 15.949$.

That our results do not differ more is probably due to the fact that the errors in the method used by Messrs. Cooke and Richards are in opposite directions and tend to neutralise each other.

BRYN MAWR, PA., *April*, 1888.

[1] Professor Cooke has recently determined the value of the error caused by the change in volume of the glass globe. He finds the corrected atomic weight of oxygen to be 15.869. This result, it seems to me, is undoubtedly too low. In my preliminary experiments (Ber. d. chem. Ges. **20**, 2323), before the precaution was taken to remove traces of nitrogen by exhausting the tube containing the palladium hydrogen, nearly the same figure was obtained, viz. 15.872.

VIII.—ON SOURCES OF ERROR IN DETERMINA-TIONS OF NITROGEN BY SODA-LIME AND MEANS FOR AVOIDING THEM.

By W. O. Atwater.

[Concluded from p. 209.]

Loss by Dissociation and Oxidation of Ammonia.

It is frequently urged that in the determination of nitrogen with soda-lime, ammonia may be dissociated at the temperature at which the combustions are conducted, and that in aspirating air through the tube at the end of the operation some of the ammonia may be burned. The following experiments were made in the hope of getting light upon the conditions under which such loss may thus occur in determinations as ordinarily made.

For this purpose means were taken to test the effects of (1) unusually long exposure of the ammonia to heat, (2) very high heat, and (3) exclusion of air. Ammonia was furnished by ammonium sulphate in which the ammonia had been determined by distillation by the method described by Gooch,[1] two determinations giving respectively 21.11 and 21.14, and averaging 21.13 per cent. of nitrogen. About 0.3 gram mixed with from 0.5 to 1.0 gram of oxalic acid previously proven to be free from nitrogen were employed in each of the determinations detailed beyond. The soda-lime, made from 1 part of caustic soda and 2½ of lime, and the method of charging the tube, were as previously described.[2] The method, which is that usually followed in this laboratory, involves filling the tube quite full of soda-lime, so as to avoid large open spaces which become filled with gases and allow long sojourn of ammonia in the tube. Where the long tubes were used, the length of the anterior layer of coarse fragments of soda-lime was increased with the length of the tube, the length of mixture of soda-lime and nitrogenous substance and the charging otherwise remaining the same as in the tubes of ordinary length. The time of combustion, about 30 to 35 minutes, was naturally a little less than would usually be the case with animal tissues. The flames

[1] This Journal **1**, 450. [2] Ibid. **9**, 319.

were turned off at the close of the combustion before the aspiration with air to wash out the ammonia. In No. 10 (see Table II) the air was expelled before the combustion, and the ammonia washed out at the end by carbonic acid. In Nos. 11 to 19 the expulsion of air and cleaning out of ammonia were effected by a current of hydrogen which was delivered by a generator so arranged as to permit easy regulation of the flow. The hydrogen was passed over heated copper foil, to remove the oxygen, before entering the combustion tube.

Five series of trials were made. Previous experience had persuaded us that when (1) the tubes are of moderate length and compactly filled with soda-lime, (2) only a moderately high heat is used, (3) the combustion does not proceed too slowly, and (4) the flames are turned off and the tube allowed to cool slightly before aspirating with air, there is no considerable loss of nitrogen by either dissociation or oxidation. In the first series, in which the operation was conducted in the usual way, a confirmation of this impression was sought. In the second series the effect of increasing the length of the tube and with it the time of sojourn of the ammonia gas in the tubes, without increasing the heat, was observed. In the third series the effect of high heat was tested by using long tubes as in the second series, and making the heat much greater. In the fourth series it was sought to learn whether the loss of nitrogen observed in the third series was due to dissociation or to oxidation, or to both. The trials of the fifth series had a similar object. The results are given in detail in Table II, which includes all the determinations made, and are recapitulated in Table III.

The figures of the first series indicate that with tubes of our ordinary length, 40 cm. or a little less, compactly filled (about 16 cm. with mixture of fine soda-lime and substance, 4 cm. with "rinsings" of fine soda-lime, and 12 cm. with an anterior layer of coarse soda-lime), at a heat sufficient to make the tube dull red, designated here as "medium," and with aspiration by air after the tubes had begun to cool, there was no loss of nitrogen.

In the second series the tubes were long enough to make the anterior layer of coarse soda-lime about 35–40 cm.; the charging otherwise was the same as in the first series. The percentage of nitrogen obtained was the same. Lengthening the tube had no effect upon the result. At moderate heat there was no loss by dis-

TABLE II.

Determinations of Nitrogen in Ammonium Sulphate under Different Conditions.

By distillation, 21.11 and 21.14, average 21.13 per cent.

By Soda-lime.

Series.	No.	Length of Tube, cm.	Heat.	Aspirated with.	Nitrogen found. Per cent.		
					Separate Determinations.	Average.	Range of Variation.
1st	1	42	Medium.	Air.	21.12		
	2	42	"	"	21.10		
	3	35	"	"	21.13	21.12	.03
2d	4	75	"	"	21.11		
	5	75	"	"	21.12		
	6	75	"	"	21.11		
	7	75	"	"	21.12	21.12	.01
3d	8	75	High.	"	20.80		
	9	75	"	"	20.86	20.83	.06
4th	10	75	"	Carbonic acid.	20.91		
	11	75	"	Hydrogen and pump.	20.70		
	12	75	"	" "	20.81		
	13	75	"	" "	20.84		
	14	75	"	" "	20.90	20.83	.21
5th	15	75	Medium.	" "	21.10		
	16	75	"	" "	21.10		
	17	75	"	" "	21.12		
	18	75	"	" "	21.11		
	19	75	"	" "	21.13	21.11	.03

TABLE III.

Recapitulation of Determinations of Nitrogen in Ammonium Sulphate under Different Conditions.

Series.	Length of Tube and Anterior Layer of Soda-lime.	Heat of Combustion.	Aspirated with.	Nitrogen found.		Loss of Nitrogen in per cent. of total Nitrogen.	
				Average.	Range of Variation.	Maxim'm.	Aver'ge.
				Per cent.	Per cent.	Per cent.	Per ct.
1st.	Usual.[1]	Medium.	Air.	21.12	0.03	...	...
2d.	Very long.[2]	Medium.	Air.	21.12	0.01	...	...
3d.	Very long.[2]	High.	Air.[3]	20.83	0.06	1.5	1.4
4th.	Very long.[2]	High.	Hydrogen.	20.83	0.21	2.0	1.4
5th.	Very long.[2]	Medium.	Hydrogen.	21.11	0.03	...	...

[1] Tube about 40 cm., anterior layer of soda-lime about 12 cm.

[2] Tube 75 cm., anterior layer about 35-40 cm.

[3] In one case with carbonic acid.

sociation with closely packed tubes even when the latter were very long and the exposure of the ammonia to the heat was increased.

In the third series the conditions were the same as in the second except that the temperature was made as high as the tubes, of the most difficultly fusible Bohemian glass we could obtain, would endure without bursting. The standard acid employed was rather concentrated, so that but a small quantity was needed in the nitrogen bulb and the internal pressure was thus reduced to a minimum. It was thus possible to heat the tubes to bright redness without their bulging. Instead of 21.12, only 20.83 per cent. of nitrogen was obtained. This falls short of the actual amount by 0.29 per cent. of the weight of the sulphate of ammonia, or 1.4 per cent. of the total nitrogen. The indication of loss by either decomposition or oxidation of ammonia was very apparent.

In the fourth series the conditions were the same as in the third except that air was excluded, the object being to find, if practicable, how much of the loss in the previous series was due to the burning of ammonia by the oxygen of the air, and how much to dissociation. In No. 10 the length of the tube was actually 80 cm. instead of 75 cm., as in the other cases. The extra 5 cm. of the posterior end were filled with bicarbonate of soda, which was heated at the beginning of the experiment to expel the air present in the tube, and again at the end to drive out the residual ammonia. In Nos. 11 to 14, as in all of the next series, in which hydrogen was used for the same purpose, the tubes were about 80 cm. long or a little longer, the extra 5 cm. at the posterior end being filled with asbestos. The hydrogen, which had been dried by sulphuric acid, was passed through the combustion tube for three quarters of an hour, and the tube was then exhausted by a mercury pump, after which hydrogen was again passed through for half an hour. Assuming that the air had thus been very nearly all removed, the combustion was conducted at the very high heat, as in the third series. When it was done, hydrogen was again passed through to wash out the residual gases, precautions being taken to admit no air. The amount of nitrogen obtained averaged the same as in the third series, 20.83 per cent. The exclusion of air made, then, no difference in the result. This indicated that the loss was due not to oxidation, but to dissociation of ammonia.

It is observable, furthermore, that the individual results in the third and fourth series vary considerably, the range in the fourth

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series being .21, while in the first and second series it was only .03 per cent. While the agreement of duplicates is a very uncertain evidence of the correctness of an analysis, a wide disagreement may be regarded as a tolerably sure indication of error.

In the fifth series the conditions were the same as in the fourth, except that the combustion was made at "medium" heat. The results, which average 21.11 per cent., are practically identical with each other and with those of the first and second series. The difference in conditions between this and the fourth series, like that between the second and third, is simply one of heat, and that difference in each case evidently makes the whole of the difference in result.

To resume :—In every case in which the medium heat was employed, whether with long or with short tubes, whether with or without air, the full amount of nitrogen was obtained. In every case with the high heat there was a loss from 1 to 2 per cent. of the total nitrogen in the substance. Neither the length of the tubes nor the presence or absence of air made any difference in either the amount of nitrogen obtained or the uniformity of the results, but the high heat materially reduced the amount of nitrogen and made wide variations in results of duplicate determinations.

That more definite statements as to temperature at which the dissociation takes place are to be desired, goes without saying. Ramsay and Young,[1] in a series of very interesting experiments on the temperature of dissociation of ammonia, find that the point at which it commences varies greatly with the nature of the surrounding medium. In a porcelain tube filled with broken pieces of porcelain, in an iron tube filled with porcelain, and in a glass tube filled with ignited "porous" asbestos cardboard to expose the gas to a large surface, the decomposition commenced at about 500° or below. At 500°–520°, however, it was very small, but increased greatly at higher temperatures. In contact with a glass surface the temperature at which decomposition begins was much higher. The nature of the surface heated has a very great influence on the amount of ammonia decomposed. In a plain dry iron tube the decomposition was apparently complete at 780°, but if water was present, only 95 per cent. was decomposed. At 760°, in a glass tube containing iron wire, 74.3—76 per cent. of the ammonia was decomposed ; but when copper was substituted (the other condi-

[1] J. Chem. Soc. 1884, Proc. p. 88.

tions remaining essentially unaltered), only 2.0 per cent. was decomposed. The authors find that "the amount of decomposition depends partly upon the rate of passage of the gas, or in other words, on the time of exposure to heat," and that "the extent of surface also influences the amount of decomposition."

From these results, as well as from consideration of what is known of dissociation in general, it is evidently impossible to predicate anything definite regarding the amount of decomposition that would take place at a given temperature in a glass tube containing soda-lime and such a complex mixture of gases as occur in an ordinary combustion. I regret the lack of facilities which prevented determinations of the temperature at which the combustions in these experiments were made. But so far as one can judge from observation, I should say that what I have here designated as "medium heat" or "usual heat," namely, that in which the combustion tube is dull red and the soda-lime yellowish, is about that at which combustions are very commonly made in the laboratories where I am acquainted.

Prehn and Hornberger[1] have reported observations which imply large losses of nitrogen by oxidation in soda-lime combustions. When sugar was burned in the tube to expel the air before the combustion and to sweep out the ammonia afterwards, considerably more ammonia was obtained than where this precaution was omitted, and the apparent oxidation by the air present in the tube at the beginning was greater than that from the air used in the aspiration at the end. But the experiments were made with ammonium salts, and where no sugar was used there was apparently no gas to drive out the air and prevent its oxygen from acting on the ammonia. In ordinary combustion of nitrogenous materials large quantities of gases are produced, and in the experiments I have just described oxalic acid was used, which naturally drove out the air.

On the other hand, numerous analysts[2] find that with proper precautions there is no loss from oxidation. In our work we have taken pains to have the tubes well filled with soda-lime and substance so as to leave only very little open space for air, and to heat the anterior layer of soda-lime before applying the heat to the mixture of soda-lime and substance, thus expelling a large part of

[1] Landw. Vs. St. **24**, 21.

[2] e. g. vid. Gruber, Zeitschr. Biol. **16**, 374, and Johnson and Jenkins, this Journal **1**, 77.

the air in advance, and have been careful not to aspirate with air until after putting out the flames so that the contents of the tube have become somewhat cooled before the air has been admitted. In how far omission of these precautions may explain the apparent oxidation elsewhere observed, I of course cannot say. Naturally there would be the less danger of loss the more the air is removed by diluting gases before heating. But considerable experience has left me with the very strong impression that with the precautions I have suggested there need be very little fear of oxidation. This must be especially true where, as in ordinary combustions, large amounts of hydrocarbons are present to combine with the oxygen.

Makris has shown that oxidation may take place, but his experiments were made under conditions especially arranged to insure admixture of air with ammonia at a high temperature.[1]

Prehn and Hornberger have also experimented upon the effect of different degrees of heat on the ammonia in determinations with ammonium salts and potassium ferrocyanide. They find, at what they call ordinary heat or dull redness, no considerable indications of dissociation, but on heating to bright redness they found with tubes 35–40 cm. and the anterior layer of soda-lime 15 cm. long, considerable, and with tubes 55–65 cm. and the anterior layer 30–40 cm. still more indication of the dissociation of ammonia. Their results thus agree with those above given, except that they get more dissociation with the high heat in the long than in the short tubes. This they very reasonably explain by the fact that the ammonia in the long tubes had more time to dissociate, from which I infer that the gases were caused to pass more slowly than was the case in our work.

Makris also tested the dissociation of ammonia by passing a slow current of gas through a tube 70 cm. long filled with pieces of soda-lime and heated to bright redness. Analysis of the gases coming from the tube showed a very considerable amount of dissociation. But, as Gruber has observed, the case here was different from that in an ordinary combustion, in that a large amount of ammonia was exposed for a long time to a high heat and without any considerable amount of diluting gas, whereas in ordinary combustion there is less free space in the tube and that largely filled with other gases, so that the ammonia is rapidly swept away, and furthermore the

[1] Ann. Chem. (Liebig) **184**, 376.

diluting gases are largely hydrocarbons which would naturally furnish nascent hydrogen to regenerate dissociated ammonia.

My results above detailed accord very exactly with those of Gruber and of Johnson and Jenkins above cited, who found no indications of loss by dissociation. But it is evident that both the complete transformation of nitrogen into ammonia, and the loss of ammonia, depend largely upon the manipulation. Thus Kissling gets very good results with an anterior layer 35 cm. long, and evident loss of nitrogen when the anterior layer is only from 7 to 10 cm. long, the combustion being carried on slowly.[1]

The experiments described by Mr. Ball and myself in a previous article[2] bear upon the questions of dissociation of ammonia and of incomplete ammonification of nitrogen of distillation products. They were made with casein, the conditions being varied so as to allow in some cases very little, and in others considerable opportunity for the ammonia formed to be dissociated. The results, given in detail in the article referred to, are more concisely set forth in Table IV, herewith.

TABLE IV.

Effects of long heating and of open space in tube upon amounts of nitrogen obtained as ammonia from casein containing 12.43 *per cent. of nitrogen.*

Conditions of Experiments.	Nitrogen Lost.					
	In per cent. of Weight of Casein.			In per cent. of Total Nitrogen.		
	Maximum.	Minimum.	Average.	Maximum.	Minimum.	Average.
	%	%	%	%	%	%
No channel, long heating (2½ hours).	0.47	0.16	0.35	3.8	1.3	2.8
Channel, ¾ hour....................	1.92	0.05	0.65	15.4	0.4	5.2
Channel, long heating.................	2.95	0.00	0.68	23.7	0.0	5.5
Channel, long heating, high heat.....	...	...	8.51	...	...	68.5
Channel, long heating, long tube.....	9.88	9.29	9.58	79.5	74.7	77.0

When the tubes were closely packed so as to insure the maximum of contact between the gases produced and the heated soda-lime (water-vapor at high temperature), and the combustion was conducted at a moderate heat and kept within the usual time of about three quarters of an hour, the full amount of nitrogen, 12.43

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[1] Ztschr. anal. Chem. **24**, 1885, 448. [2] This Journal **10**, 113.

per cent. of the water-free casein, was obtained as ammonia. But when the combustion proceeded very slowly so as to occupy two and a half hours, the other conditions remaining the same, only from 12.27 to 12.08 per cent. of nitrogen were obtained as ammonia, making a loss of from 0.16 to 0.47 per cent. reckoned on the weight of the water-free casein, or from 1.3 to 3.8 per cent. of the total nitrogen. It seems reasonable to ascribe this loss to dissociation during the long time that the ammonia was exposed to the heat, though possibly some of it may have been due to incomplete ammonification of nitrogenous decomposition products. It is easy to understand how the ammonia passing rapidly through the interstices between the particles of soda-lime in the closely packed tube, in the ordinary analyses, would be so mixed with water-vapor and other gases that the nitrogenous distillation products would be completely changed to ammonia, and in the very brief exposure to heat the resultant dissociation would be too small to be noticeable. On the other hand, when the operation extends through two and a half hours instead of three quarters of an hour, it would seem by no means improbable that the anterior layer of soda-lime might, before the end of this long period during which it is kept hot, cease to give off any considerable amount of water-vapor. But it is probably this water-vapor which yields the hydrogen to form ammonia with the nitrogen of the volatile distillation products, and it is not impossible that the same vapor may also tend by its presence to prevent dissociation of ammonia. Add the fact that, when the operation goes on slowly, the time of sojourn of the ammonia in the heated tube is of course relatively much longer than the increased time of combustion would imply, and a large loss by dissociation and incomplete ammonification is easy to understand.

When a channel was left in the tube so that the contact between distillation products and soda-lime was less intimate, the loss of nitrogen was still greater. When, with the channel, the combustion occupied only three quarters of an hour, this loss varied from 0.4 per cent. to 15.4 per cent. of the total nitrogen. But when the combustion, with the channel, was prolonged to two and a half hours, the loss reached in one case 27 per cent. of the total nitrogen. This increased loss would seem most probably due to both incomplete ammonification and dissociation. At any rate, the conditions provided for less perfect contact between soda-lime and sub-

stance ; for reduction of the supply of moisture which would pro-
vide hydrogen for ammonification and would also tend to prevent
dissociation ; and for a very long exposure of ammonia to heat.

When, with channel and long heating as before, the temperature
of combustion was raised as high as the tubes would endure, the
loss was very much greater and amounted to 68.5 per cent. of the
total nitrogen. The most natural explanation of this increased
loss is the increased dissociation of ammonia. When the length
of the anterior layer of soda-lime was increased, and with it, conse-
quently, the amount of open space inside the tube, the loss of
nitrogen was greater still, namely, from 75 to 79 per cent. of the
whole.

It would, of course, be foolish to attempt to say how much of
the loss in these latter cases was due to dissociation and how much
to incomplete ammonification. Such questions can be answered
only by more detailed experiments in which the gases produced
should themselves be analysed. But it does seem reasonably safe
to say that both dissociation and incomplete ammonification must
account for a large part, if not all, of the errors here observed, and
that there is great danger of loss in these ways unless due precau-
tions are observed.

To conclude : As regards loss by dissociation and oxidation,
the facts above cited appear to warrant the inferences that, in
combustions conducted by the method here described, in which
(1) the tubes were so closely packed with soda-lime as to leave a
minimum of free space inside, (2) full opportunity was provided
for contact between distillation products and soda-lime (water-
vapor at high temperature) by the anterior layer of soda-lime 12
cm. long or thereabouts, which was well heated before applying
the heat to the mixture of soda-lime and substance, and main-
tained at a medium heat during the whole operation, and (3) the
operation was completed in not over three quarters of an hour :

1. Provided the tube and contents are allowed to cool slightly
before aspirating with air, there need be no loss by oxidation.

2. At a temperature sufficient to heat the tube only to dull
redness, there need be no considerable loss by dissociation.

3. Ammonia may be dissociated and nitrogen lost by either
very high heat, or by conducting the operation so slowly as to
leave the ammonia exposed for a long time to heat. Very likely
the danger of long exposure is heightened by lack of moisture

from the anterior layer of soda-lime after the latter has been heated for some time.

4. A vacant space in the tube (channel as ordinarily recommended) may involve serious loss. This loss is probably due to both incomplete ammonification of distillation products and to dissociation of ammonia.

The danger of loss of ammonia from rapid flow of the gases through the acid solution in the bulb-tube is sometimes assumed to be considerable. Musso, for instance, lays great stress upon uniform and slow evolution of gas, and prolongs the combustion for several hours, the main purpose seeming to be to insure complete absorption of the ammonia.[1] The experiments cited by Mr. Haynes in a previous article[2] imply that the real danger from this source is very small. All his attempts to push the combustion fast enough to force ammonia through the solution were ineffectual. For instance, in a combustion of sulphate of ammonia, completed in 12 minutes, the ammonia, which was sufficient to neutralise half or a little over half of the acid, was entirely absorbed. The volume of the acid solution was 10 cc. ; it was contained partly in the bottom bulb and partly in the outer bulb of an ordinary Knop and Arendt bulb apparatus, in accordance with our usual practice.

Bearing of the Results upon the Interpretation of those obtained by other Experimenters. The Difficulties with the Soda-lime Method observed by Seegen and Nowack, Musso, and others.

Of the investigations which have been interpreted as casting doubt upon the reliability of the soda-lime method, those of Seegen and Nowack have perhaps been the most frequently quoted. These have carried great weight because the figures obtained were so wide of the truth despite the evident pains taken to secure accurate results, and because similarly bad results have been obtained by other chemists. The apparently unavoidable sources of serious error in the soda-lime method have been alleged as a ground for doubting the correctness of important series of researches in which the soda-lime method has been used. The question of the validity of this doubt is a very important one.

In his account of his own experiments with flesh, Nowack states that care was taken to insure uniform development of gas, and the

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[1] Ztschr. anal. Chem. **16**, 414.　　　　[2] This Journal **10**, 111.

tubes were kept glowing hot for three hours ("die Röhre stets durch 3 Stunden glühen ").[1] In the report of their joint experiments with animal and vegetable protein compounds, albumin, casein, syntonin, flesh, gluten, legumin, Seegen and Nowack state that they employed the same analytical methods and precautions ("die Analysen wurden in derselben Weise und mit denselben Cautelen ausgeführt, die . . . ausführlich erörtert sind ") as were employed by Nowack in his own investigations just referred to.[2] The inference is that their combustions were likewise continued through a long time, if not at a high temperature. Musso, whose experiments were made with milk, whey, and cheese, says his combustions lasted hardly less than three hours, and in some cases they were prolonged for even six hours.[3] In the work of Nowack, of Nowack and Seegen, and of Musso, the figures obtained for nitrogen were very small. Taking those for nitrogen obtained by the absolute method as the standard, the loss of nitrogen in Nowack's experiments reached 20 per cent. and even more of the whole nitrogen; in those of Seegen and Nowack the loss was from 1 to 20 per cent., while in those of Musso it was over 30 per cent. of the whole nitrogen.

[1] Sitzungsber. d. Weiner Akad. **64**, Math.-Nat. Classe, II, 1871, 362. Dr. Nowack, in the article referred to, says as follows: "Weiter unterleiss ich niemals mich durch Prüfung mittelst sehr empfindlicher rother und blauer Lackmuspapiere von der genauen Neutralisation zu überzeugen, da bei einer noch so langsamen geleiteten Verbrennung von Fleisch mit Natronkalk die Will-Varrentrapp'sche Vorlage durch die entstandenen Distillationsprodukte sich derart färbt dass das Betüpfen eines sehr empfindlichen Lackmuspapieres das Erkennen der Neutralisationsgrenze viel deutlicher anzeigt, als die Beobachtung der Endreaction in der missfarbigen Flüssigkeit. . . . Bei der Ausführung der Verbrennung mittelst Natronkalk sorgte ich für den regelmässigen Gang der Gasentwickelung, liess die Röhre stets volle drei Stunden glühen, steigerte namentlich in der zweiten Hälfte der Verbrennungsdauer die Hitze so hoch als möglich und endete nicht früher als bis der Natronkalk Spuren von Schmelzung zeigte, und an seiner Oberfläche keine schwärzlichen Kohlenpartikeln mehr, sondern nur eine graulichweisse Farbe wahrnehmbar war."

The article by Dr. Nowack, from which the above is cited, was preceded by one by Prof. Seegen (loc. cit., 11, 63, 11), ("Zur frage über die Ausscheidung des Stickstoffs der im Körper zersetzten Albuminate," in which he says the nitrogen was determined in flesh by elementary analysis with copper oxide and "durch Glühen mit Natronkalk in dazu vorbereiteten, starken, etwa ½ Meter langen Verbrennungsröhren." The results with soda-lime were all lower than the lowest with copper oxide. That the nitrogen was not all converted into ammonia Prof. Seegen shows by the fact that "als ich den Glührückstand mit Wasser verrieb und das Ganze neuerdings der Glühhitze unterzog, es wurden beim zweiten Glühen stets noch grössere oder geringere Mengen von NH_3 in der Will'schen Vorlage nachgewiesen, und ausserdem zeigte der zweite Glührückstand einen ganz exquisiten Geruch nach Methylamin." On another page Prof. Seegen says that Dr. Nowack had made a number of nitrogen determinations in flesh, which were to be published later, referring, evidently, to those in the article by Dr. Nowack, above cited; and adds, "Die Arbeit ist mit grösster Sorgfalt, mit Beobachtung aller Cautelen und Berücksichtigung jeder Fehlerquelle ausgeführt."

[2] Pf. Archiv. **7**, 1873, 290.

[3] Ztschr. anal. Chem. **16**, 1877, 414.

On the other hand, Gruber, who in reply to the criticism of Seegen and Nowack upon analyses by Voit and others in Munich, gives very satisfactory results obtained in Voit's laboratory with protein in flesh, never allowed more than an hour for the combustions.

The experiments cited by Mr. Woods and myself in article No. IV of this series seem to us to give satisfactory assurance of the reliability of soda-lime determinations of nitrogen in ordinary protein compounds when the combustions were made with proper precautions. Of the latter the chief seem to us to be (1) sufficiently fine pulverisation and careful mixture of the substance with soda-lime ; (2) close packing of the tube and sufficiently long anterior layer of soda-lime, so as to insure sufficient contact between soda-lime (heated water vapor) and distillation products, as well as to avoid too long sojourn of ammonia in the heated tube ; and (3) maintaining the anterior layer at a moderate heat during the whole time of combustion, which should not be too protracted.

Messrs. Seegen and Nowack do not state whether they left a channel in their tubes or not, but it is evident that the conditions of their work were such as to favor incomplete decomposition of the nitrogenous substance, imperfect ammonification of volatile decomposition products, and dissociation of ammonia. Prof. Seegen reports a nitrogenous residue in the tube after the combustions, and Dr. Nowack found the acid solutions in the nitrogen bulbs so highly colored as to interfere with titration with litmus solution. The combustion was prolonged for three hours and during part of this time at a very high heat. The determinations of Muss were conducted very slowly, in some cases even more so than those of Seegen and Nowack, and the results obtained were likewise very low. Mr. Ball and I found that either leaving a channel in the tube, or high heating, or prolonging the combustion to two and a half hours, involved large loss of nitrogen, the loss with these conditions combined amounting, in some cases, to two thirds or three fourths of the whole nitrogen.

It would seem, therefore, that we have here cases of a kind not unfrequent in scientific research, in which the very effort to secure correct and reliable results involves grievous error.

I lay especial stress upon this matter because of the use that has been made of Seegen and Nowack's results to discredit the soda-lime method in general, and particularly to throw doubt upon the

work of Voit and others in the Physiological Laboratory at Munich, in which this method has been employed in the study of the fundamental problems of nutrition. It was my fortune some time since, while working in that laboratory, to be permitted to observe very closely the ways in which determinations of nitrogen by soda-lime are there conducted. Although the effort to insure close packing of the tubes was perhaps less than in the experiments above detailed, and upon which the conclusions here given are based, yet on the whole the details of manipulation as I observed them were such as would, with the experience in this laboratory, lead one to expect correct results.

Although the results of experiments by Gruber and others in the Munich laboratory, and accumulated experience elsewhere, make any vindication of its work superfluous, yet I trust these statements, in connection with an explanation of the error into which Seegen and Nowack have unwittingly fallen, may, in the interests of science, not seem out of place.

The experience of other chemists, as well as that in this laboratory, of which part has been described in these pages, leaves me with the decided belief that the Scylla and Charybdis of the soda-lime determination are incomplete ammonification of nitrogenous distillation products and dissociation of ammonia. The other difficulties are, in general, easy to overcome. They may all be prevented, in ordinary animal and vegetable protein compounds, by the precautions above enumerated. But in alkaloids and allied compounds, and in some amines, and amido and azo-compounds, loss by incomplete ammonification seems very difficult to avoid.

The observations I have had occasion to make, as well as printed accounts of the methods followed in different laboratories, have given me the decided impression that the most common difficulties are loose packing of the combustion tube so as to leave a channel, insufficient anterior layer of soda-lime, and too high or too long-continued heating.

The soda-lime method is beset with dangers and requires great care to avoid them. Indeed, after the experience in this laboratory, covering a period of several years and including some thousands of nitrogen determinations, if I were going to undertake again a series of analyses like those for which these studies were made, and the details of the work were to be placed in the hands of an analyst, however expert, who had not been through some such

experience as that above described, I should feel under the necessity of asking him to do a considerable amount of preliminary work, including comparison of results by the soda-lime with other methods, before I could feel sure of his results. A case in point may be worth mentioning.

After most of the above detailed experiments had been made and we had the method in such control that we were wont to say jocosely that from a given protein compound we could obtain the whole or any desired fraction of the nitrogen as ammonia, at will, a gentleman of no little experience, and who afterwards proved himself a skillful and efficient analyst, came to our laboratory as assistant. We placed a number of substances, mostly animal tissues, in his hands for nitrogen determinations by the soda-lime method, instructing him in the details of the process, and going through a number of determinations with him. He was very confident that he could secure perfectly reliable results and at the same time make the determinations with considerable rapidity. After a list of substances had been analysed I looked over his figures and was somewhat surprised at the variations in the duplicate determinations, which in some cases, as I now recall, reached nearly 0.2 per cent. This led me to question their accuracy. Mr. Woods, by whom most of the nitrogen determinations of this investigation have been made, repeated the analyses and found in almost every case a considerably higher percentage of nitrogen, so that the whole work had to be repeated. The most plausible explanation of the errors seemed to be that the determinations in question were made rather hurriedly, and either because the nitrogenous material was not well enough mixed with the soda-lime, or from too loose packing of the tube, some of the nitrogenous distillation products were incompletely ammonified and thus escaped detection in the titration subsequent to combustion.

At the same time I must repeat what I have already said, that our experience leads me to place the greatest confidence in the soda-lime method for the determination of nitrogen in ordinary protein compounds, provided the work be conducted with the precautions here insisted upon.

The perfection to which Kjeldahl's method has lately been brought, and its accuracy, convenience, and inexpensiveness, have led to its use in this as in many other laboratories. Our experience leads us to decidedly prefer it to the soda-lime method, though we find it advantageous to use both, making one check the other.

But the danger of incomplete ammonification of some classes of compounds, *e. g.* alkaloids, makes us feel it necessary to control both by the absolute method for all classes of substances except those for which they have been most thoroughly tested.

SUMMARY.

The experimental and other considerations presented in this and the previous articles on the determination of nitrogen by soda-lime, may be conveniently summarised, after first recalling the probable reaction by which the nitrogen is changed to ammonia, and the principal sources of error in the operation.

1. It seems decidedly probable that the change of nitrogen to ammonia is effected by union, at high temperature, with water vapor yielded by the soda-lime (or slaked lime in case the latter is used). It is essential that the contact between nitrogenous distillation products and water vapor be sufficient and at not too high or too low temperature to insure conversion of all the nitrogen to ammonia, and that the ammonia be not dissociated or oxidised. The main objects, then, are to secure complete ammonification and to avoid dissociation and oxidation.

2. The chief difficulty in the way of complete ammonification of protein compounds appears to be the formation of gases which do not readily yield their nitrogen to be united with the hydrogen of the water vapor. With certain other classes of nitrogenous compounds, as leucine and its congeners, alkaloids, amines, and amido and azo-compounds, this difficulty is greater and sometimes apparently insuperable. The tendency of protein compounds to be decomposed by heat and other agencies into leucine, amines, etc., appears to explain the difficulty frequently found in getting all their nitrogen into the form of ammonia by heating with soda-lime. The evident means to secure complete ammonification must be sufficient contact with soda-lime at proper temperature.

3. The danger of dissociation of ammonia evidently increases with increase of temperature and time of exposure, and is probably diminished by presence of water vapor and other diluting gases. If this be so, the danger will be avoided by measurably rapid combustion at not too high heat, and by keeping the ammonia in contact with sufficient moisture from the soda-lime until it leaves the heated tube.

4. Leaving out of account substances such as nitrates, nitro-compounds, etc., whose nitrogen is imperfectly converted into

ammonia by soda-lime, even in the presence of organic matter, and assuming palpable errors of manipulation to be avoided, such as (*a*) loose packing of asbestos plug, which would allow particles of soda-lime to be swept into the acid bulb; (*b*) heat at anterior end of the tube so low as to permit ammonia to be retained with moisture about the cork, or so high as to char the cork and give rise to acid or alkaline distillation products; (*c*) use of soda-lime containing nitrates or nitrites, which may, according to circumstances, either furnish nitrogen to be transformed into ammonia or oxygen to burn the ammonia formed from the nitrogen of the substance; (*d*) use of distilled water containing ammonia for rinsing the acid bulb; (*e*) imperfectly cleaned or incorrectly calibrated burettes; the principal sources of error above discussed involve loss of nitrogen, and may be recapitulated thus:

I. Loss from imperfect ammonification of the nitrogenous substance, due to:—

a. Incomplete decomposition of the substance, part of the nitrogen being, from coarseness of the particles of the substance, imperfect mixing with the soda-lime, insufficient heat, or other cause, left behind in the charred residue.

b. Change of nitrogen into compounds other than ammonia, either such as may remain in the tube, *e. g.* cyanogen; or volatile distillation products which escape ammonification and pass through the acid solution unabsorbed, or, if absorbed, are not accurately determined by the titration or other means used to find the amount of nitrogen in the solution.

c. Escape of nitrogen in the free state.

II. Loss of ammonia through:—

a. Dissociation at high heat in the combustion tube.

b. Oxidation by air present in the tube before, or introduced in aspirating to wash out ammonia after, the combustion.

c. Neutralisation by acid products, *e. g.* of sugar, where the latter is used in the combustion.

d. Incomplete absorption by the acid solution.

5. Complete decomposition of the substance has, in our experience, been readily secured by pulverisation fine enough for it to pass through a sieve of 1 mm. aperture; thorough mixing with soda-lime; avoiding the shaking by which the particles gather at the top of the soda-lime; and heating to low redness.

6. With sufficient soda-lime, not too dry, we have found no reason to fear the formation of cyanides, nor have we been able

to obtain any indication of the escape of free nitrogen when the operation is properly conducted, although it might, perhaps, occur by oxidation of ammonia if there were nitrates or nitrites present, or if aspiration with air were done while tube and contents are hot. Turning off the flame before aspirating has, in our experience, sufficed to avoid oxidation by air. At least, if ammonia has been oxidised, the quantity has been too small to be detected.

7. When sugar is used, acid products may be formed in quantities large enough to impair the accuracy of the determinations. With ordinary animal and vegetable protein compounds, provided enough soda-lime is employed, the use of hydrogen, or sugar, or other substances for supplying gases, either to expel air, or to yield nascent hydrogen to form ammonia with the nitrogen, or to dilute the ammonia and prevent dissociation, or to wash out the ammonia, appears to be unnecessary. The danger of loss by incomplete absorption of the ammonia by the acid solution appears to be very small indeed, even when the development of gases is very rapid, provided sufficient acid solution be used.

The chief sources of loss appear to be from incomplete ammonification and from dissociation of the ammonia formed.

8. The first of these two difficulties is a serious one. With protein compounds, the great trouble is evidently the formation of volatile decomposition products which do not readily yield their nitrogen to form ammonia with hydrogen. This is easy to understand when we consider that protein compounds are prone to yield cleavage products such as leucine and its congeners, compounds allied to the alkaloids, amido-compounds, etc.; and that it is very difficult to get all the nitrogen of these latter into the form of ammonia with soda-lime, evidently because of their proneness to form compounds that resist the ammonifying action.

With alkaloids and allied compounds, leucine and other amido-compounds, amines, and azo- and nitro-compounds, complete ammonification is not always effected even with the utmost care. Concerning peptones our experience does not enable us to speak. But for the protein of ordinary animal and vegetable substances, including casein, proper precautions appear to insure complete ammonification of the nitrogen. The important condition appears to be sufficient contact with heated soda-lime (*i. e.* with water vapor at high temperature).

This contact is best secured by (*a*) intimate mixture of substance with soda-lime; (*b*) close packing so as to avoid open space inside

the tube; (*c*) providing a reasonably long anterior layer of soda-lime; (*d*) heating this latter to dull redness before bringing the heat to bear upon the substance, and keeping it hot until the combustion is done.   In order to insure the maximum of surface for contact it is well to have the anterior layer consist of coarse particles of soda-lime containing enough lime to prevent fusing together.   It is possible that too long heating may result in expelling the water from the soda-lime, so that there will not be enough in the latter part of the operation to insure complete ammonification.

Though it is desirable to avoid coloration and turbidity of the acid solution, these do not necessarily imply incomplete ammonification, nor does their absence prove perfect combustion.   With proper care to insure contact between soda-lime and substance, we have almost never found the solution so colored as to seriously interfere with titration.

9. Ammonia may be dissociated and nitrogen lost by either too high heating, or by conducting the operation so slowly as to leave the ammonia exposed for a long time to heat.   It seems probable that the presence of water vapor, as of other gases, would tend to prevent dissociation of the ammonia, and that the danger of long heating may be partly due to reduced supply of moisture from the anterior layer of soda-lime after the latter has been heated for some time.

10. A vacant space in the tube (channel as ordinarily recommended) may cause serious loss.   This loss is greater the higher the temperature and the longer the time of combustion.   It is probably due not only to incomplete ammonification of distillation products through lack of contact with the soda-lime, but also to dissociation of ammonia.   With the channel the flow of the gases is slower and they are exposed to heat longer than when the tube is packed full.   Add the possible lack of water vapor when the heating is long continued and the loss by dissociation is very clearly explained.   When the tube is closely packed, the flow of gases reasonably fast, and the operation conducted at a temperature sufficient to heat the tube only to dull redness, there appears to be no considerable loss by dissociation, even with a long anterior layer (20 or 30 cm.) of soda-lime.

Concerning reagents, apparatus and manipulation, a few words will suffice.

1. *Soda-lime.*—The soda-lime made by mixing one part of ordinary caustic soda with two and a half parts of quicklime by the process described,[1] costs very little for materials and labor, and serves the purpose very satisfactorily. In sifting it is conveniently divided into a finer portion to be mixed with the substance, and into coarser particles to be used for the anterior layer. It bears heating without fusing so much as to leave any considerable open space in the tube if closely packed at the outset. Varying proportions of soda-lime, from 1 part to $2\frac{1}{2}$ parts of lime to each part by weight of soda, have made no difference in the results of the analyses. We have obtained equally good results with the mixture of sodium carbonate and slaked lime as described by Johnson, and see no reason why slaked lime as recommended by him should not be generally efficacious as it has proven in the cases cited by him and in those tried by ourselves. Our reason for adhering to the ordinary soda-lime has been the impression that by filling the anterior portion of the tube with coarse particles of the rather difficultly fusible material, more complete contact is insured between nitrogenous distillation products and the heated water vapor from the soda-lime. The old theory that enough soda should be mixed with the lime to make the mixture easily fusible does not stand the test of experience.

In testing the purity of soda-lime by sugar, as is sometimes recommended, there is danger of error both from the presence of nitrogen in the sugar and from formation of acid distillation products.

2. *Tubes and charging.*—For ordinary combustions, tubes of from 35 to 40 cm. in length do very well. The method of charging the tube upon which we have gradually settled after numerous trials with tubes of different lengths and charged in different ways, is explained in the accompanying tabular statement :

Length of tube	40 cm.
Asbestos and fine soda-lime . . .	4 "
Mixture, fine soda-lime and substance .	16 "
Rinsings, fine soda-lime . . .	4 "
Anterior layer, coarse soda-lime . .	12 "
Asbestos, open space, plug . . .	4 "

With a shorter tube the divisions may be made proportionately shorter. We intend to have at least 40 parts by weight of fine

[1] This Journal **9,** 312.

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soda-lime for every part of substance in the "mixture." About 0.4 and 0.6 of flesh (water free), or corresponding amounts of other materials, we find convenient. The importance of fine pulverisation of substance, intimate mixture with soda-lime, filling the tube compactly so as to have no channel, avoiding the shaking by which particles of the substance might be brought to the top of the soda-lime, and heating until no charred material is left, has been dwelt upon. An anterior layer of coarse soda-lime, 12 centimeters long, has proven very satisfactory. The anterior layer should be well heated before the heat is applied to the mixture of soda-lime and substance, and kept hot until the combustion is done.

3. *Heat and time of combustion.*—A "low red" heat ordinarily suffices. Heating to bright redness brings danger of loss of ammonia by dissociation, though in our experience, when the tube is closely packed and the operation not too slow, we have found practically no difficulty in getting all the nitrogen as ammonia even at high heat. But with a channel in the tube the loss by high heating has been considerable.

Ordinarily, three quarters of an hour is ample for the combustion, and an hour the extreme limit, according to the experience in this laboratory. Rapid combustion is less and long heating more dangerous than is frequently taught. With an ordinary Knop and Arendt (four bulb) bulb apparatus containing 10 cc. of acid solution, of which little over half was required to neutralise the ammonia, the ammonia was completely absorbed even when the combustion lasted only twelve minutes. Serious loss may result from too long heating, especially if there be open space in the tube or the temperature is high.

4. *Determination of the ammonia.*—In the combustion of ordinary protein compounds with the precautions stated above, practically all the nitrogen is converted into ammonia, and its determination by titration is easy. We find it well, however, to use concentrated solutions and to avoid excess of water in rinsing out the bulbs. The quantity of concentrated acid solution required is small and the tension in the combustion tube during the heating consequently slight, which is a convenience; while, with the small quantity of solution in titrating, the color reaction is sharp and the determination easy and accurate. Freshly prepared cochineal solution is the most satisfactory indicator we have found. Very narrow burettes, in which 10 cc. occupy from 30 to 40 cm., have decided advantages for convenience and accuracy when concentrated solutions are used.

LIX.—ON TRIBROMTRINITROBENZOL.[1]

By C. Loring Jackson and John F. Wing.

The following paper contains the description of the first results of a research on tribromtrinitrobenzol and its derivatives, which we are obliged to publish now, as on account of the departure of one of us from Cambridge we cannot go on with the work together. Had it not been for this, we should have postponed its publication until our experiments on the reduction of triamidotrinitrobenzol had led to some definite result. At present we are able to describe only the tribromtrinitrobenzol, triamidotrinitrobenzol, and trianilidotrinitrobenzol, with several preliminary experiments on other substances which we mention in order to reserve the further study of this subject for one of us, who will continue it in this laboratory.

The tribromtrinitrobenzol has never been described, for although Koerner[2] in 1874 stated that he had obtained it by the action of a mixture of boiling fuming nitric and sulphuric acids on tribromdinitrobenzol, he gave no description of it, saying that this must be postponed till a later paper. Some years afterward (in 1879) Wurster and Beran,[3] after many attempts to prepare the substance according to Koerner, came to the conclusion that it could not be made in this way, as, even when Koerner's mixture of acids was heated with tribromdinitrobenzol to 220° in a sealed tube, they got only a very small amount of a substance melting from 200° to 220°, the greater part of the product being unaltered tribromdinitrobenzol. As this paper has remained unanswered by Koerner up to the present time, that is, for eight years, we have assumed that he has abandoned the subject, and have accordingly taken it up, our attention being called to it by the results obtained in the study of the action of nitric acid on trichlorbenzol described in a previous paper.[4] Upon treating symmetrical tribrombenzol with a mixture of fuming sulphuric acid and a nitric acid of specific gravity 1.51, but essentially free from nitrous fumes, we found, as

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] Gazz. chim. ital. 1874, 425.

[3] Ber. d. chem. Ges. **12** (1879), 1821.

[4] This Journal **9**, 348.

stated in the paper just mentioned, that tribromtrinitrobenzol was formed, thus confirming the results of Koerner, in opposition to those of Wurster and Beran; and in the same place we have tried to show that the most probable cause of the failure of these latter chemists to obtain tribromtrinitrobenzol was the presence of a large quantity of nitrous fumes in the nitric acid used by them, which raised its specific gravity without increasing its strength.

Tribromtrinitrobenzol, $C_6Br_3(NO_2)_3$.

Symmetrical tribrombenzol (melting point 119°) was converted into tribromdinitrobenzol, either by treatment with nitric acid[1] of specific gravity 1.51, the mixture being warmed to secure complete action, or by boiling it with a mixture of commercial fuming nitric acid and common sulphuric acid. To convert the tribromdinitrobenzol, by whichever process prepared, into tribromtrinitrobenzol, 20 grams of it were dissolved by the aid of heat in a mixture of about 500 cc. of the nitric acid of specific gravity 1.51 mentioned above with one third of its volume of fuming sulphuric acid, since these proportions had been found by experiment to give the best result with the least consumption of acid, and the solution boiled gently in a flask loosely closed with a glass bulb. As a portion of the nitric acid volatilises during the boiling, a little of the solid separates, which can be dissolved by the addition of more nitric acid, but this precaution is not necessary in working on a large scale. When the mixture had boiled for four to five hours it was allowed to cool, and then, disregarding the comparatively large amount of solid which had separated, poured into snow, and the precipitate washed thoroughly with water and afterward purified— first by extraction with hot alcohol, which removed the unaltered tribromdinitrobenzol, since the tribromtrinitrobenzol is but slightly soluble even in hot alcohol—and then by crystallisation from chloroform, which separated the less soluble tribromtrinitrobenzol from the tetrabromdinitrobenzol[2] which was always formed at the same time. The crystallisation from chloroform was continued until the substance showed the constant melting point of 285°; it

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[1] Prepared directly from sulphuric acid and nitre, not pushing the reaction beyond the formation of acid potassic sulphate. See our previous paper, this Journal 9, 348.

[2] The purification and identification of this substance are described at the end of this paper. If the tribromtrinitrobenzol is to be used in making triamidotrinitrobenzol it is not necessary to purify it completely from tetrabromdinitrobenzol.

was then dried at 100°, and its composition determined by the following analyses:[1]

I. 0.2310 gram of the substance gave 19.6 cc. of nitrogen under a pressure of 765 mm. and a temperature of 21°.

II. 0.1688 gram of the substance gave, according to the method of Carius, 0.2128 gram of argentic bromide.

	Calculated for $C_6Br_3(NO_2)_3$.	Found. I.	II.
Nitrogen	9.33	9.72	
Bromine	53.33	...	53.64

The yield was far from satisfactory, amounting on the average from about 15 to 20 per cent. of the theoretical, although on one occasion we obtained 40 per cent. As, however, the tribromdinitrobenzol used in this case was the residue from the alcoholic extracts derived from previous preparations, we think that a considerable part of this large yield consisted of tribromtrinitrobenzol from the previous processes, which had been dissolved by the hot alcohol, since, although nearly insoluble in hot alcohol, it is not completely so. It follows from this that it is well to use the tribromdinitrobenzol obtained in purifying the crude product with alcohol as material for a new preparation.

Properties.—The tribromtrinitrobenzol forms good-sized, well developed white crystals, with perhaps a slight yellowish tinge, which differ in habit according to the solvent from which they have been crystallised. From benzol, hexagonal prisms terminated by hexagonal pyramids are deposited, which look very much like some forms of quartz crystal; from a mixture of benzol and alcohol, long, slender, tapering prisms are obtained, which under the microscope seem to be made up of rows of hexagonal pyramids united as in cap quartz, so that the edges of the prisms are bluntly serrated; crystallised from chloroform, the prisms are not so slender as from benzol and alcohol, and the twinning just described is much better marked. These crystals, furrowed by numerous re-entering angles parallel to the basal plane, are very characteristic. The substance melts at 285° (uncorr.), and sublimes to a slight extent when heated in an air-bath, even at as low a temperature as 175°. It is but slightly soluble in alcohol, even when boiling, essentially insoluble in it when cold, soluble in chloroform, and more easily in ether, benzol, acetone, glacial acetic acid, or

[1] See also page 287.

carbonic disulphide. Chloroform, or a mixture of benzol and alcohol, is the best solvent for it.

The tribromtrinitrobenzol is a decidedly reactive substance, forming compounds with most of the common reagents; of these compounds we have been able to study thoroughly only those derived from alcoholic ammonia and aniline, which will be described later in the paper, but some preliminary experiments with other reagents may find a place here. With potassic hydrate, dissolved in alcohol, a yellow product was formed which gave red potassium and yellow·barium salts, the latter being only slightly soluble, and separating in hair-like crystals from its hot aqueous solution. It is probable that this product is the trinitrophloroglucine of Benedikt,[1] but to decide this point the experiment must be repeated with a larger quantity of substance. With sodic ethylate it gives what appears to be a new compound. When boiled with an alcoholic solution of potassic sulphocyanate it forms a dark red powder, which we have not yet succeeded in obtaining in crystals. When heated in a sealed tube with potassic iodide and alcohol to 150° for 18 hours, a crystalline compound is formed which has a very high melting point and explodes when heated to a somewhat higher temperature; but the yield is so small that we have not been able as yet to obtain enough of it sufficiently pure for analysis. All these substances will be more thoroughly studied in this laboratory, and the behavior of tribromtrinitrobenzol with other reagents, especially sodium malonic ester, will be investigated also. When tribromtrinitrobenzol is heated to 100° with common strong sulphuric acid, it dissolves, but crystallises out unaltered as the solution cools. A boiling solution of argentic nitrate in alcohol has no action on it, and the same remark applies to argentic nitrite, as was to be expected. We hope, however, that the triiodtrinitrobenzol may react with this latter substance, and it was for this reason that we undertook the study of the action of potassic iodide on the tribromtrinitrobenzol.

In the hope of obtaining addition products similar to those formed by Hepp's trinitrobenzol with hydrocarbons, we have studied the action of tribromtrinitrobenzol on naphthaline. For this purpose benzol solutions of the two substances were mixed in the proportion of one molecule of each, but we obtained from the mixed solutions only crystals melting at 285°; as, however, the

[1] Ber. d. chem. Ges. **11**, 1376.

melting tubes contained a slight sublimate, and the habit of the crystals was somewhat different from that of tribromtrinitrobenzol, we thought it possible, although not probable, that a compound might have been formed which decomposed before it melted, and have accordingly analysed the crystals, which, remembering the instability of Hepp's substance, were dried only by pressing between filter paper, in order to be certain that the substance should not be decomposed.

0.1200 gram of the substance gave, according to the method of Carius, 0.1500 gram of argentic bromide.

	Calculated for $C_6Br_3(NO_2)_3$.	Found.	Calculated for $C_6Br_3(NO_2)_3C_{10}H_8$.
Bromine	53.33	53.20	41.52

It is evident, therefore, that the substance is only tribromtrinitrobenzol, and that it does not combine with naphthaline under these conditions. The same negative result was obtained when chloroform or ether was substituted for benzol as the solvent. We may add, too, that the tribromtrinitrobenzol shows no tendency to unite with benzol, so far as we could find.

Triamidotrinitrobenzol, $C_6(NH_2)_3(NO_2)_3$.

When tribromtrinitrobenzol is mixed with cold alcoholic ammonia, an action sets in almost immediately, as shown by the appearance of an orange color in the solution; and, if the substances are allowed to stand for twelve hours in a corked flask at ordinary temperatures, the reaction proceeds further, but is not complete, as is shown by the presence of white specks consisting of unaltered tribromtrinitrobenzol in the undissolved solid. It is necessary, therefore, in order to bring this small amount of unaltered substance into the reaction, to boil the mixture in a flask with a return condenser for about half an hour, adding more alcoholic ammonia as it is needed. The nearly insoluble triamidotrinitrobenzol is then filtered hot from the orange liquid, which has the color of a strong solution of potassic dichromate,[1] and the paler yellow solid purified by washing, first with water to remove ammonic bromide, and afterward with alcohol to get rid of the organic impurities.

The triamidotrinitrobenzol can be made conveniently also from the mixture of tribromtrinitrobenzol and tetrabromdinitrobenzol

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[1] Our study of the substances contained in this liquid is not complete as yet, but a description of the results obtained up to this time will be found on page 290.

obtained in purifying tribromtrinitrobenzol, thus utilising directly a secondary product which could be separated into its pure constituents only with a great outlay of time and work. For this purpose the mixture is treated with alcoholic ammonia in the manner already described when speaking of the preparation from pure tribromtrinitrobenzol, and the product freed from the tetrabromdinitrobenzol, which is not attacked by alcoholic ammonia under these conditions, by boiling and washing with benzol or chloroform after the washing with alcohol.

The composition of the substance after being dried at 100° was determined by the following analyses:

I. 0.2352 gram of the substance gave on combustion 0.2370 gram of carbonic dioxide and 0.0544 gram of water.

II. 0.2346 gram of the substance gave 0.2342 gram of carbonic dioxide.[1]

III. 0.2186 gram of the substance gave 60.4 cc. of nitrogen under a pressure of 770 mm. and a temperature of 19°.

IV. 0.1058 gram of the substance gave 29.6 cc. of nitrogen under a pressure of 765 mm. and a temperature of 20°.

	Calculated for $C_6(NH_2)_3(NO_2)_3$:	I.	II.	III.	IV.
Carbon	27.90	27.48	27.23		
Hydrogen	2.32	2.57			
Nitrogen	32.55	...	...	32.19	32.22

Properties.—As obtained from the action of alcoholic ammonia on the tribromtrinitrobenzol, the triamidotrinitrobenzol forms an amorphous powder of an orange or yellow color, according to the conditions under which it was prepared; crystallised from aniline or nitrobenzol, it forms small rhombic plates of a pale yellow color. It decomposes without melting above the boiling point of mercury, and is nearly, although not completely, insoluble in water, alcohol, ether, benzol, chloroform, or glacial acetic acid. It dissolves in aniline, or in nitrobenzol, and, as already stated, can be obtained in crystals from these solutions. Cold strong sulphuric acid slowly dissolves it, forming a pale yellow solution, but on dilution the unaltered substance is precipitated. Dilute sulphuric acid, or dilute or strong nitric or hydrochloric acid, has no action on it, and when the substance was suspended in alcohol and hydrochloric acid gas passed into the liquid no change was observed. It is therefore

[1] The hydrogen of this analysis was lost.

either incapable of forming salts, or can form them only under unusual conditions. When the solution in strong sulphuric acid was heated it became charred.

We have made many attempts to convert the triamidotrinitrobenzol into an acet-compound, but have found that it was not acted on by glacial acetic acid, acetylchloride, or acetic anhydride, even when sealed with the substance and heated to 150°; we infer, therefore, that the radical acetyl cannot be introduced directly into the molecule.

The reduction of triamidotrinitrobenzol naturally has engaged our attention, as by this means it might be possible to obtain hexamidobenzol. Owing to want of material, however, our experiments on this subject have not been brought to a conclusion, but we think it best to describe them briefly now, as we shall have no other opportunity to put them in print, if the future work of one of us on this subject should not lead to the desired result; and there seems to be only too much reason to fear that this will be the case, especially since Nietzki and Hagenbach[1] have found that ammonia is eliminated in reductions which should lead to pentamidobenzol. Up to this time we have tried only three reducing agents, tin and hydrochloric acid, ammonic sulphydrate in alcoholic solution, and zinc dust and acetic acid. The first of these, tin and hydrochloric acid, removed ammonia from the molecule, as was proved by the formation of pink salt and the precipitation of ammonic chlorplatinate on adding chlorplatinic acid, the latter being analysed for still greater certainty. This was the result whether tin and hydrochloric acid or stannous chloride and hydrochloric acid were used. The alcoholic solution of ammonic sulphydrate gave a more promising result; but, as it was evident that the product was decomposed at a temperature a little above that at which it was formed, we turned our attention to the third method, which seemed on the whole the most promising, since zinc dust and 80 per cent. acetic acid acting in an atmosphere of carbonic dioxide seem to reduce the triamidotrinitrobenzol completely; at any rate the yellow color disappears and the whole goes into solution. This solution, after being freed from zinc with sulphuretted hydrogen, gave no precipitate with sodic hydrate, nor did ether extract anything from the alkaline solution. It was blackened by exposure to the air even more readily than a solution of a salt of diamido-

[1] Ber. d. chem. Ges. **20**, 331. See also p. 2114.

benzol, and the residue from it was decomposed easily by heat; chlorplatinic acid gave no precipitate with it, but chlorauric acid threw down an uninviting precipitate which we thought was in part at least a product of oxidation. If the substance formed was really hexamidobenzol, it is evident that its isolation in a form fit for analysis will be a matter of great difficulty owing to its extreme instability. The study of this subject will be continued in this laboratory, however, as soon as a sufficient quantity of material can be prepared, and the work will be extended also to the action of other reducing agents, including those which form azo-compounds.

As yet we have been unable to finish the study of the substances contained in the orange-red filtrate formed in the preparation of the triamidotrinitrobenzol, because, in spite of its marked color, the amount of solid dissolved in it is far from large. It seems, however, to contain at least two compounds, one crystallising in red needles, frequently grouped in round masses like chestnut burs, the other a yellow substance forming flat crystals; but the separation of these two bodies is a matter of such great difficulty that we have not yet succeeded in obtaining either of them in a state of purity, nor are we certain that these are the only secondary products of the reaction.

Trianilidotrinitrobenzol, $C_6(NHC_6H_5)_3(NO_2)_3$.

This substance was prepared by allowing a mixture of tribromtrinitrobenzol and aniline, in the proportion of one molecule of the former to six of the base, to stand at ordinary temperatures, when the reaction runs slowly, but is complete after the mixture has stood for a day or two. The product was purified by washing with water to which a little hydrochloric acid was added to remove any slight excess of free aniline, and crystallising the residue from a mixture of alcohol and chloroform. It was dried at 100°, and analysed with the following results:

I. 0.1468 gram of the substance gave on combustion 0.3176 gram of carbonic dioxide and 0.0516 gram of water.

II. 0.1830 gram of the substance gave 28.1 cc. of nitrogen at 25° temperature and 755 mm. pressure.

	Calculated for $C_6(NHC_6H_5)_3(NO_2)_3$.	Found. I.	II.
Carbon	59.26	58.99	
Hydrogen	3.71	3.90	
Nitrogen	17.28	...	17.02

If an excess of aniline is used in the preparation and the mixture heated, a coloring matter is formed looking like rosaniline ; but the purification of this substance was attended with such great difficulties that we have abandoned for the present the further study of this reaction, in which the nitro groups undoubtedly play a part.

Properties.—The trianilidotrinitrobenzol forms an orange powder, crystallising from alcohol or chloroform in fine red needles which melt at 238°. It is essentially insoluble in water, soluble with difficulty in alcohol, but easily in chloroform, soluble in ether, benzol, glacial acetic acid, or acetone. The best solvent for it is a mixture of alcohol and chloroform. Hydrochloric acid has no action on it, and in general it shows no more tendency to form salts than the corresponding amido compound. Strong nitric acid produces no change of color when added to it.

Tetrabromdinitrobenzol, $C_6Br_4(NO_2)_2$.

As has been already stated, during the preparation of the tribromtrinitrobenzol from tribromdinitrobenzol by the action of nitric acid and fuming sulphuric acid there was formed invariably another substance which melted in the crude state at about 230°, and was left behind with the tribromtrinitrobenzol after the tribromdinitrobenzol was removed with alcohol, and was separated partially from it by crystallising the residue from chloroform, in which the trinitro compound is less soluble than the other substance. In this way it is easy to get the trinitro compound in a state of purity ; but to purify completely the other substance it is necessary to submit the residue from the evaporation of the chloroform mother-liquors to systematic fractional crystallisation from a mixture of alcohol and benzol, which removes a small quantity of tribromtrinitrobenzol. These crystallisations lowered the melting point instead of raising it, as is usual, and after it had been brought down from about 230° to 224° it remained constant, and then the substance, dried at 100°, was analysed with the following results :

I. 0.3526 gram of the substance gave 18.7 cc. of nitrogen at 24° temperature and 764 mm. pressure.

II. 0.1690 gram of the substance gave, by the method of Carius, 0.2606 gram of argentic bromide.

	Calculated for $C_6Br_4(NO_2)_2$.	Found. I.	Found. II.
Nitrogen	5.78	5.97	
Bromine	66.11	...	65.62

These analyses and the melting point 224° prove that the substance is the tetrabromdinitrobenzol, melting point 227°–228°, discovered by von Richter.[1]

The following experiments were tried to throw light upon the manner in which the tetrabromdinitrobenzol was formed. In the first place, to prove that it was not formed from an impurity (tetrabrombenzol) in our tribrombenzol, we have prepared it from an analysed sample of tribromdinitrobenzol. This experiment was hardly necessary, as the tribrombenzol and tribromdinitrobenzol used by us in working on the large scale showed the correct melting points within two degrees; but we felt that absolute certainty on this point was important, and accordingly prepared some perfectly pure tribromdinitrobenzol, melting point 190° (von Richter[2] gives 191°, Koerner[3] 192°), which gave on analysis the following result:

0.1658 gram of the substance gave, according to the method of Carius, 0.2314 gram of argentic bromide.

	Calculated for $C_6Br_3(NO_2)_2H$.	Found.
Bromine	59.26	59.39

This was treated with a mixture of nitric acid and fuming sulphuric acid, precisely as in the preparation of tribromtrinitrobenzol, and yielded a product which, after removing the unattacked tribromdinitrobenzol, consisted of tribromtrinitrobenzol and tetrabromdinitrobenzol in about equal parts, thus proving that the tetrabromdinitrobenzol is not derived from an impurity, but is formed during the process.

A second experiment had for its object to determine whether the conversion of the tribromdinitrobenzol into tetrabromdinitrobenzol was due to the fuming sulphuric acid, which might well be the case, since Bässmann[4] has observed that symmetrical tribrombenzol is converted in part into pentabrombenzol when heated with fuming sulphuric acid to 100° from a week to a fortnight. We accordingly heated another quantity of the pure tribromdinitrobenzol with an excess of fuming sulphuric acid in a sealed tube to 100° for twelve hours, but no tetrabromdinitrobenzol was formed, and, as the temperature of our mixture during the manufacture of the tribromtrinitrobenzol could have been little, if at all, above 100°,

[1] Ber. d. chem. Ges. **8**, 1427.
[3] Gazz. chim. ital. 1874, 425.
[2] Ber. d. chem. Ges. **8**, 1426.
[4] Ann. Chem. (Liebig) **191**, 208.

and that process was carried on for only five hours, we are inclined to ascribe the formation of the tetrabrom compound to the nitric rather than the sulphuric acid.

In a third experiment the mixture of tribromdinitrobenzol with nitric and fuming sulphuric acids was boiled for only a quarter of an hour, instead of for the usual five hours, and the proportion of tetrabromdinitrobenzol formed was comparatively small, it would seem, therefore, that it is formed chiefly in the later part of the boiling ; but it is not advantageous in preparing tribromtrinitrobenzol to diminish the length of the boiling, as the superior purity of the product does not compensate for the much smaller yield. We may add that another experiment showed that it was impossible to convert tribromtrinitrobenzol into tetrabromdinitrobenzol by boiling it with the mixture of nitric acid and fuming sulphuric acid.

Von Richter, the discoverer of tetrabromdinitrobenzol, gave the melting point 227°–228°, whereas our substance showed a constant melting point of 224°. We are of the opinion, however, that von Richter's melting point is more correct than ours, as it might well be that a small quantity of tribromtrinitrobenzol, sufficient to lower the melting point 4°, could not be removed by crystallisation, and in fact our analysis seems to indicate the presence of such an impurity ; but as our object was to identify the substance rather than study its properties, we did not think it worth while to sacrifice the large amount of time and labor which would undoubtedly have been necessary to settle this point thoroughly. Von Richter also states that it is soluble in alcohol or benzol, and Bodewig[1] has published a thorough description of its crystalline form. The following properties, which we have had occasion to study, have not been published heretofore, so far as we can find. It begins to sublime at about 175°, and is soluble in methyl alcohol, ether, acetone, glacial acetic acid, or carbonic disulphide ; the best solvent for it is a mixture of alcohol and benzol, in the former of which it is but sparingly soluble. It dissolves in cold sulphuric acid, but is precipitated unchanged on dilution. When heated over a free flame with sulphuric acid it is destroyed. The bromine in it is much more firmly attached to the molecule than in the tribromtrinitrobenzol, as it is not removed when the substance is boiled with alcoholic ammonia in open vessels. It is also very hard to

[1] Ztschr. Kryst. **3**, 398.

effect its complete decomposition in its analysis according to Carius.

Finally, we may remark that it is highly probable that the substance melting above 200° obtained by Wurster and Beran by heating tribromdinitrobenzol to 220° in a sealed tube with a mixture of fuming nitric and sulphuric acids was the tetrabromdinitrobenzol.

LX.—SILICOTETRAFLUORIDES OF CERTAIN BASES.[1]

By Arthur M. Comey and F. W. Smith.

Supplementary to the investigations[2] made by C. Loring Jackson and one of us on the action of fluoride of silicon on organic bases, we have further tried the action of fluoride of silicon on nitrosodimethylaniline, pyridine, cinchonine, and quinine.

Trinitrosodimethylaniline disilicotetrafluoride, $(C_8H_{10}N_2O_3)_3$ $(SiF_4)_2$.—This compound was formed by passing fluoride of silicon through a solution of the base in benzol. A lemon-yellow precipitate was formed, which was washed thoroughly with benzol and dried at 100°. The following results were obtained from the analysis of this product:

0.1822 gram of the substance gave 0.0345 gram of silicic dioxide and 0.0936 gram of sodic fluoride.

	Calculated for $(C_8H_{10}N_2O_3)_3(SiF_4)_2$.	Found.
Silicon	8.54	8.83
Fluorine	23.09	23.25

Trinitrosodimethylaniline disilicotetrafluoride is a bright yellow amorphous powder which is decomposed by water, with separation of silicic dioxide, and decomposes completely with slight explosion when heated above 150°.

Dipyridine silicotetrafluoride, $(C_5H_5N)_2SiF_4$.—This substance was prepared by passing fluoride of silicon through a solution of pyridine in benzol, whereupon it separates out in the form of a heavy voluminous precipitate, which when washed with benzol and dried, and immediately analysed, gave the following results:

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] This Journal **10,** 165.

0.3132 gram of the substance gave 0.0925 gram of silicic dioxide and 0.2039 gram of sodic fluoride.

	Calculated for $(C_5H_5N)_2SiF_4$.	Found.
Silicon	10.77	10.81
Fluorine	29.00	29.45

Dipyridine silicotetrafluoride is a pure white amorphous powder which decomposes upon standing, giving off pyridine and forming tripyridine disilicotetrafluoride.

Tripyridine disilicotetrafluoride, $(C_5H_5N)_2(SiF_4)_2$.—This compound is formed by subliming the previous substance. Pyridine is given off and tripyridine disilicotetrafluoride sublimes, forming a crust possessing a distinct crystalline structure. It is extremely deliquescent and was not obtained in a pure state for analysis. The following results of the analysis of the slightly deliquesced substance leave no doubt as to its true constitution.

0.1743 gram of the substance gave 0.0443 gram of silicic dioxide and 0.1248 gram of sodic fluoride.

	Calculated for $(C_5H_5N)_3(SiF_4)_2$.	Found.
Silicon	12.68	11.86
Fluorine	34.14	32.16

When fluoride of silicon was passed into the ethereal solutions of *cinchonine* or *quinine*, a gummy substance separated which probably possessed a constitution similar to that of the above substances.

The constitution of these substances has been discussed at length in a previous paper[1] by C. Loring Jackson and one of us. It remains only to add that the compounds of which dianiline silicotetrafluoride is the type seem to be formed first. These are very unstable, giving up one molecule of the base with the greatest ease to form compounds corresponding to trianiline disilicotetrafluoride. This extra molecule of the base in most cases is separated by merely washing with a solvent as benzol, as in the case of aniline, toluidine, diphenylamine, chinoline, etc. In others, as dimethylamine and pyridine, the extra molecule is only given off upon standing, or by the action of heat.

Boron trifluoride gave products with organic bases which apparently possess an analogous constitution, but the substances formed were not further investigated.

According to Schiff,[1] stannic tetrachloride forms an addition product with aniline, of the composition $(C_5H_7N)_4SnCl_4$. With diphenylamine, however, we obtained by the action of stannic tetrachloride a product, melting at 180°–181°, containing no tin; chlorine was present in large quantity. The investigation of the action of stannic tetrachloride on organic bases will be continued by one of us.

The above work was done in the Summer School of Chemistry at Harvard College.

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ON THE ACTION OF PHOSPHORUS PENTACHLORIDE ON THE THREE ISOMERIC MONO-HYDROXY-BEN-ZOIC ACIDS.[2]

By Richard Anschütz and George D. Moore.

After a brief account of earlier work on the subject of the action of phosphorus pentachloride on salicylic acid, the authors begin the account of their own experiments.

I. *The action of a single molecule of phosphorus pentachloride on salicylic acid: Formation of the chloride o-*$C_7H_4Cl_3PO_3$.

As raw material we employed exclusively salicylic acid, which was thoroughly dried by several days' standing over sulphuric acid in desiccators. We brought but one molecule of phosphorus pentachloride into reaction with one molecule of salicylic acid, the experience of Couper and others having shown that any excess over this amount was superfluous, and we were thus further enabled to follow the reaction step by step. We found that the reaction runs very easily of itself. After the evolution of hydrochloric acid is finished, there remains a light yellow liquid, which we at once distilled in a vacuum. We found that, as Drion and Couper had

[1] Jsb. Chem. 1863, 412.

[2] Abstract of papers which appeared in the Annalen der Chemie, Vol. 228, page 308, Vol. 239, pages 314 and 333, and were afterwards communicated to this Journal by the authors. For the analytical details see the original articles.

stated, only a very small amount of phosphorus oxychloride was formed. As soon as this was distilled off, the temperature rose rapidly until, under a mercury pressure of 11 mm., a clear, colorless, highly refractive liquid distilled over, constant at 168°, only a relatively small amount of a dark colored syrup remaining behind. Drion's statement that the product of the action of phosphorus pentachloride on salicylic acid is not volatile without decomposition, even under diminished pressure, is therefore a mistake. The analyses of this liquid, purified by several distillations, and finally boiling quite constant at 168° under 11 mm. pressure, gave figures in accordance with the formula $C_7H_4Cl_3PO_2$.

If to one equivalent of salicylic acid rather more than one equivalent of phosphorus pentachloride be employed, a much better yield of the chloride $o\text{-}C_7H_4Cl_3PO_3$ is obtained.

If the chloride $o\text{-}C_7H_4Cl_3PO_3$ be treated with water, it behaves differently according to the amount of water employed. If a small quantity of water be poured over it, the mixture gradually becomes warm, and finally gives a clear solution; from this solution only salicylic acid crystallises out on cooling. If, on the other hand, a large amount of water is added to the chloride, and the mixture be shaken thoroughly, cooling if necessary, until solution results, the liquid thus obtained gives no reaction for salicylic acid : it is only after several days' standing that this reaction can be observed. If, however, the solution, prepared in the cold and with a large amount of water as above described, *be boiled*, the products are salicylic, phosphoric and hydrochloric acids.

Inasmuch as the first product of an excess of water upon the chloride evidently contained phosphorus, and constituted a body which yielded salicylic acid, we attempted to isolate it by quick evaporation in a vacuum. We obtained in this manner a white, amorphous substance, free of chlorine but containing phosphorus, which melted at about 147° and was almost entirely soluble in a small amount of water. There remained undissolved in this case a few fine white needles, which the addition of ferric chloride solution at once proved to be salicylic acid.

It is evidently impossible to obtain the above-mentioned product in a state of absolute purity, owing to the readiness with which, in the presence of water, it goes over into salicylic acid. An analysis showed it to have the composition $C_7H_7PO_6$.

If the chloride $o\text{-}C_7H_4Cl_3PO_3$ be treated with one equivalent

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of water in the shape of anhydrous oxalic acid, two chlorine atoms are replaced by one of oxygen, and a compound of the formula $o\text{-}C_7H_4ClPO_4$ results, the reaction being :

$$o\text{-}C_7H_4Cl_3PO_3 + C_2O_4H_2 = o\text{-}C_7H_4ClPO_4 + CO + CO_2 + 2HCl.$$

This substance is a white crystalline body and melts at 80°.

In order to explain the constitution of the chloride $o\text{-}C_7H_4Cl_3PO_3$ we must consider salicylic acid both as an acid and as a phenol, *i. e.* as ortho-carboxylphenol. Phosphorus pentachloride acts very readily upon the carboxyl group, forming the chlorcarbonyl group COCl. The by-products are phosphorus oxychloride and hydrochloric acid. The former reacts upon phenol, forming phenyl-ortho phosphoric acid dichloride, as Jacobsen[1] has recently shown. Salicylic acid contains both the carboxyl and hydroxyl groups : the first is attacked by the phosphorus pentachloride and gives the chlorcarbonyl group, phosphorus oxychloride and hydrochloric acid. The phosphorus oxychloride then attacks the phenol-hydroxyl and forms the group $OPOCl_2$ plus hydrochloric acid. The final product is therefore $C_6H_4 \begin{cases} (1)\ COCl^2 \\ (2)\ OPOCl_2, \end{cases}$ the reactions being :

$$C_6H_4 \begin{cases} (1)\ COOH \\ (2)\ OH \end{cases} + PCl_5 = C_6H_4 \begin{cases} (1)\ COCl \\ (2)\ OH \end{cases} + POCl_3 + HCl\ ;$$

$$C_6H_4 \begin{cases} (1)\ COCl \\ (2)\ OH \end{cases} + POCl_3 = C_6H_4 \begin{cases} (1)\ COCl \\ (2)\ OPOCl_2 \end{cases} + HCl.$$
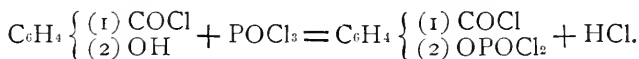
The product so obtained is Couper's "trichlorophosphat de salicyl." From the reactions it is evident why only one equivalent of phosphorus pentachloride enters into the reaction, why but little phosphorus oxychloride is formed, and why, finally, the product, if treated with a small amount of water, forms hydrochloric and salicylic acids ; with a larger quantity, on the other hand, a soluble compound, in which the salicylic acid residue doubtless plays a part similar to that of the phenol residue in the mono-phenyl-ortho-phosphoric acid. According to its constitution this

[1] Ber. d. chem. Ges. **8**, 1521.

[2] Later investigations, the preliminary results of which have already been published by Emery and one of us in a paper entitled " Über die Einwirkung von Phosphortrichlorid auf Salicylsäure" (Ann. der Chemie **233**, 301), after the completion of our research, show that in regard to the constitutional formula of the chloride $o\text{-}C_7H_4Cl_3PO_3$ which we have written $C_6H_4 \begin{cases} (1)\ COCl \\ (2)\ OPOCl_2, \end{cases}$ the formula $C_6H_4 \begin{cases} (1)\ COO \\ (2)\ O \end{cases} > PCl_3$ is also worthy of consideration. For the present, however, we prefer the first formula, suspending all judgment for or against the second until the research in connection therewith has been completed.

" trichlorophosphat de salicyl " may be designated as *ortho-chlor-carbonyl-phenyl-ortho-phosphoric dichloride.*

Two determinations of the specific gravity gave $d^{2,0}_4 = 1.55513$ and 1.55215; mean $= 1.55364$.

The action of a second molecule of phosphorus pentachloride on the chloride o-$C_7H_4Cl_3PO_3$: Formation of the chloride o-$C_7H_4Cl_5PO_2$.

If equal molecules of the chloride o-$C_7H_4Cl_3PO_3$ and phosphorus pentachloride be heated together in sealed tubes at $165°$–$170°$ until everything is dissolved, it is at once evident, from the increase in the volume of the liquid, that a reaction has taken place. On rectifying the contents of the tubes under diminished pressure, a large quantity of phosphorus oxychloride is first obtained, more or less phosphorus pentachloride subliming over at the same time. Between $165°$ and $170°$ a small amount of unchanged chloride, o-$C_7H_4Cl_3PO_3$, comes over; the principal product, however, boils at $176°$–$179°$, the pressure being 11–12 mm. For the analyses, a portion boiling constant at $178°$ under 11–12 mm. pressure was employed.

The results of the analyses show that the compound has the composition o-$C_7H_4Cl_5PO_2$. It is formed thus :

$$o\text{-}C_7H_4Cl_3PO_3 + PCl_5 = o\text{-}C_7H_4Cl_5PO_2 + POCl_3.$$
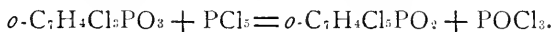
As in the case of the chloride o-$C_7H_4Cl_3PO_3$, a much better yield of this product is obtained when an excess of phosphorus pentachloride is employed.

The action of a third molecule of phosphorus pentachloride on the chloride : Formation of ortho-chlorbenzotrichloride.

Pure $C_7H_4Cl_5PO_2$ was heated with rather more than one equivalent of phosphorus pentachloride in closed tubes at about $180°$. After several days' heating all the pentachloride was dissolved and the contents of the tube consisted of a clear yellowish liquid. No pressure was manifested as the tubes were opened. The raw product was rectified under diminished pressure, and the first distillate consisted of a large quantity of phosphorus oxychloride, together with more or less pentachloride. The greater part of the remainder boiled between $135°$ and $150°$, under 13–14 mm. pressure; the last portion, however, probably unchanged $C_7H_4Cl_5PO_2$,

between 175° and 180°. On being again rectified, this fraction came over between 128° and 131° as a clear colorless liquid which, in a cooling mixture, solidified to a white crystalline mass. The analyses showed that it is ortho-chlorbenzo-trichloride, $C_7H_4Cl_4 \left(= C_6H_4 \left\{ \begin{array}{l} (1)\ CCl_3 \\ (2)\ Cl \end{array} \right. \right)$.

The following reactions express, step by step, the action of phosphorpentachloride on salicylic acid:

$$C_6H_4 \left\{ \begin{array}{l} (1)\ COOH \\ (2)\ OH \end{array} \right. + PCl_5 = o\text{-}C_7H_4Cl_3PO_3 + 2HCl;$$

$$o\text{-}C_7H_4Cl_3PO_3 + PCl_5 = o\text{-}C_7H_4Cl_5PO_2 + POCl_3;$$

$$o\text{-}C_7H_4Cl_5PO_2 + PCl_5 = C_6H_4 \left\{ \begin{array}{l} (1)\ CCl_3 \\ (2)\ Cl \end{array} \right. + 2POCl_3.$$
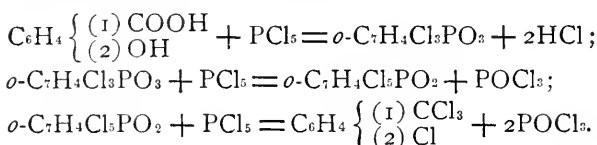
Starting from the two different constitutional formulas of the chloride $o\text{-}C_7H_4Cl_3PO_3$, we perceive that not only the chloride $o\text{-}C_7H_4ClPO_4$, but also the chloride $o\text{-}C_7H_4Cl_5PO_2$, may have one of two different constitutional formulas. All these formulas are given in the following table:

$o\text{-}C_7H_4ClPO_4$	$C_6H_4 \left\{ \begin{array}{l} (1)\ COCl \\ (2)\ OPO_2 \end{array} \right.$	$C_6H_4 \left\{ \begin{array}{l} (1)\ COO \\ (2)\ O \end{array} \right\rangle POCl$
$o\text{-}C_7H_4Cl_2PO_3$	$C_6H_4 \left\{ \begin{array}{l} (1)\ COCl \\ (2)\ OPOCl_2 \end{array} \right.$	$C_6H_4 \left\{ \begin{array}{l} (1)\ COO \\ (2)\ O \end{array} \right\rangle PCl_3$
$o\text{-}C_7H_4Cl_5PO_2$	$C_6H_4 \left\{ \begin{array}{l} (1)\ CCl_3 \\ (2)\ OPOCl_2 \end{array} \right.$	$C_6H_4 \left\{ \begin{array}{l} (1)\ COCl \\ (2)\ OPCl_4 \end{array} \right.$
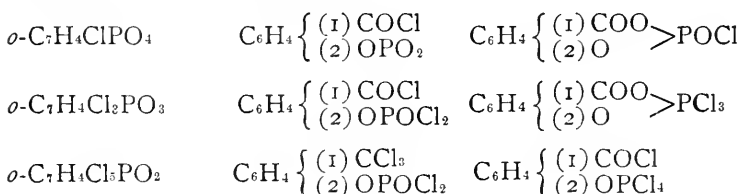
Since the chloride $o\text{-}C_7H_4Cl_5PO_2$ is easily converted by water into the acid $o\text{-}C_7H_4PO_3(OH)_3$, it would follow from the formula $C_6H_4 \left\{ \begin{array}{l} (1)\ CCl_3 \\ (2)\ OPOCl_2 \end{array} \right.$ that the ortho-oxybenzo-trichloride (a compound thus far unknown) is either incapable of existence in the presence of water, or under these conditions is easily converted into salicylic acid. The formula $C_6H_4 \left\{ \begin{array}{l} (1)\ COCl \\ (2)\ OPCl_4 \end{array} \right.$ has, thus far, its sole analogue in the compound $C_6H_5OPCl_4$.[1] The behavior of the chloride $o\text{-}C_7H_4Cl_5PO_2$ could be explained with the help of it, as well as by using the first of the above mentioned formulas.

We hope that we shall be able to explain the constitution of the chloride $o\text{-}C_7H_4Cl_5PO_2$ by the help of synthetical reactions.

[1] Ann. d. Chemie **239**, 312.

Decomposition of the chloride o-$C_7H_4Cl_3PO_3$ by distillation under ordinary pressure.

If the chloride be distilled rapidly, it conducts itself in the same way as " trichlorophosphat de salicyl," as described by Couper. At a temperature somewhat over 300°, hydrochloric acid is given off, and a liquid distills over, in which, after several days' standing in a sealed tube, large transparent crystals are deposited. These crystals melted at 80°, and in general form and appearance were identical with the product already described which was obtained by the action of anhydrous oxalic acid on the chloride o-$C_7H_4Cl_3PO_3$.

A series of elaborate experiments was now undertaken to determine the character of the decomposition of the chloride when it is distilled slowly under ordinary pressure. The products obtained were phosphorus oxychloride, o-chlor-benzoyl chloride, o-chlor-benzo-trichloride, and the compound o-$C_7H_4ClPO_4$.

It has been shown that the chloride o-$C_7H_4Cl_3PO_3$ gives, with anhydrous oxalic acid, the chloride o-$C_7H_4ClPO_4$, two chlorine atoms being replaced by one of oxygen. It is highly probable that both these chlorine atoms are attached to phosphorus, and under this assumption, the rest, PCl_2, behaves toward anhydrous oxalic acid in a manner quite similar to phosphorpentachloride :

$$Cl_3PCl_2 + (COOH)_2 = Cl_3PO + CO_2 + CO + 2HCl;$$
$$o\text{-}C_7H_4ClO_3PCl_2 + (COOH)_2 =$$
$$o\text{-}C_7H_4ClO_3PO + CO_2 + CO + 2HCl.$$
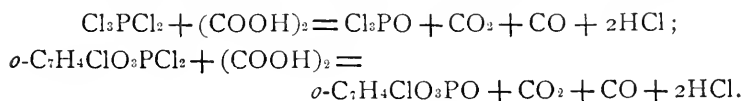
If we consider, further, that by the action of phosphorus pentachloride, the chloride o-$C_7H_4Cl_3PO_3$ is converted first, at a temperature of 160°–165°, into the chloride o-$C_7H_4Cl_5PO_2$, and this by still further action of phosphorus pentachloride at 180° into ortho-chlor-benzo-trichloride, phosphorus oxychloride being in each case the by-product, according to the reactions:

$$o\text{-}C_7H_4Cl_3PO_3 + PCl_5 = o\text{-}C_7H_4Cl_5PO_2 + POCl_3,$$
$$o\text{-}C_7H_4Cl_5PO_2 + PCl_5 = C_6H_4 \begin{cases} (1)\ CCl_3 \\ (2)\ Cl \end{cases} + 2POCl_3,$$
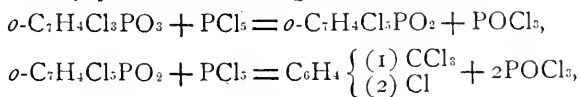
we may readily assume that the two chlorine atoms in the chloride o-$C_7H_4Cl_3PO_3$ which behave toward anhydrous oxalic acid in the same manner as the two chlorine atoms of phosphorus pentachloride, can play a similar part in other reactions, *c. g.* by heating with another molecule o-$C_7H_4Cl_3PO_3$ at high temperature. This assumption seems all the more probable from the

fact that we find a large amount of the chloride o-$C_7H_4ClPO_4$ among the decomposition products obtained by slowly heating the chloride o-$C_7H_4Cl_3PO_3$ under ordinary pressure. The chloride o-$C_7H_4ClPO_4$ takes the place of the phosphorus oxychloride formed in the phosphorus pentachloride reaction; it is formed by the replacement of two chlorine atoms of the chloride o-$C_7H_4Cl_3PO_3$ by an oxygen atom, and these chlorine atoms served for the production of the ortho-chlor-benzoyl and ortho-chlor-benzo-trichlorides, as well as of the chloride o-$C_7H_4Cl_5PO_2$ from which, by the splitting off of phosphorus oxychloride, the ortho-chlor-benzo-trichloride is formed.

The following reactions serve to explain the decomposition process which takes place when the chloride o-$C_7H_4Cl_3PO_3$ is slowly heated under ordinary pressure:

I. $\quad o\text{-}C_7H_4Cl_3PO_3 + o\text{-}C_7H_4Cl_3PO_3 =$

$$o\text{-}C_7H_4ClPO_4 + C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (2)\ Cl \end{Bmatrix} + POCl_3;$$

II. $\quad o\text{-}C_7H_4Cl_3PO_3 + o\text{-}C_7H_4Cl_3PO_3 =$

$$o\text{-}C_7H_4ClPO_4 + o\text{-}C_7H_4Cl_5PO_2;$$

III. $\quad o\text{-}C_7H_4Cl_5PO_2 + o\text{-}C_7H_4Cl_3PO_3 =$

$$o\text{-}C_7H_4ClPO_4 + C_6H_4 \begin{Bmatrix} (1)\ CCl_3 \\ (2)\ Cl \end{Bmatrix} + POCl_3.$$
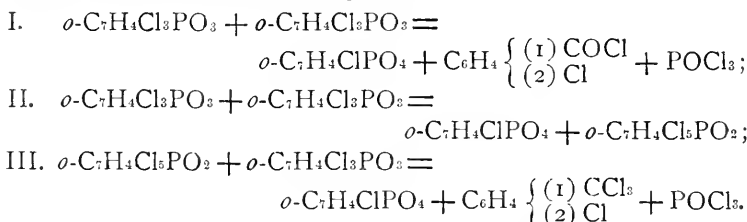
From this general formulation we see that the interpretation of the decomposition of the chloride o-$C_7H_4Cl_3PO_3$ is independent of the constitutional formulas of the phosphorus derivatives of salicylic acid. A much better idea of the course of the reactions is obtained by the use of graphic formulas. Thus, assuming the constitution of the first product of the action of phosphorus pentachloride on salicylic acid to be $C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (2)\ OPOCl_2 \end{Bmatrix}$, we may write the last three equations as follows:

I. $\quad C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (2)\ OPOCl_2 \end{Bmatrix} + C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (2)\ OPOCl_2 \end{Bmatrix} =$

$$C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (2)\ OPO_2 \end{Bmatrix} + C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (2)\ Cl \end{Bmatrix} + POCl_3;$$

II. $\quad C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (2)\ OPOCl_2 \end{Bmatrix} + C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (2)\ OPOCl_2 \end{Bmatrix} =$

$$C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (2)\ OPO_2 \end{Bmatrix} + \quad \begin{matrix} C_6H_4 \begin{Bmatrix} (1)\ CCl_3 \\ (2)\ OPOCl_2 \end{Bmatrix} \\ \text{or} \\ C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (2)\ OPCl_4 \end{Bmatrix} \end{matrix} \quad ;$$

III.
$$C_6H_4 \begin{cases} (1)\ CCl_3 \\ (2)\ OPOCl_2 \end{cases}$$
$$\text{or} \qquad + C_6H_4 \begin{cases} (1)\ COCl \\ (2)\ OPOCl_2 \end{cases} =$$
$$C_6H_4 \begin{cases} (1)\ COCl \\ (2)\ OPCl_4 \end{cases}$$
$$C_6H_4 \begin{cases} (1)\ COCl \\ (2)\ OPO_2 \end{cases} + C_6H_4 \begin{cases} (1)\ CCl_3 \\ (2)\ Cl \end{cases} + POCl_3.$$

Assuming now that the constitution of the first chloride $o\text{-}C_7H_4Cl_3PO_3$ is $C_6H_4 \begin{cases} (1)\ COO \\ (2)\ O \end{cases} > PCl_3$, we may write :

I. $C_6H_4 \begin{cases} (1)\ COO \\ (2)\ O \end{cases} > PCl_3 + C_6H_4 \begin{cases} (1)\ COO \\ (2)\ O \end{cases} > PCl_3 =$
$\qquad C_6H_4 \begin{cases} (1)\ COO \\ (2)\ O \end{cases} > POCl + C_6H_4 \begin{cases} (1)COCl \\ (2)Cl \end{cases} + POCl_3;$

II. $C_6H_4 \begin{cases} (1)COO \\ (2)O \end{cases} > PCl_3 + C_6H_4 \begin{cases} (1)\ COO \\ (2)\ O \end{cases} > PCl_3 =$
$\qquad C_6H_4 \begin{cases} (1)\ COO \\ (2)\ O \end{cases} > POCl + C_6H_4 \begin{cases} (1)\ COCl \\ (2)\ OPCl_4 \end{cases};$

III. $C_6H_4 \begin{cases} (1)COO \\ (2)O \end{cases} > PCl_3 + C_6H_4 \begin{cases} (1)\ COCl \\ (2)\ OPCl_4 \end{cases} =$
$\qquad C_6H_4 \begin{cases} (1)\ COO \\ (2)\ O \end{cases} > POCl + C_6H_4 \begin{cases} (1)\ CCl_3 \\ (2)\ Cl \end{cases} + POCl_3.$
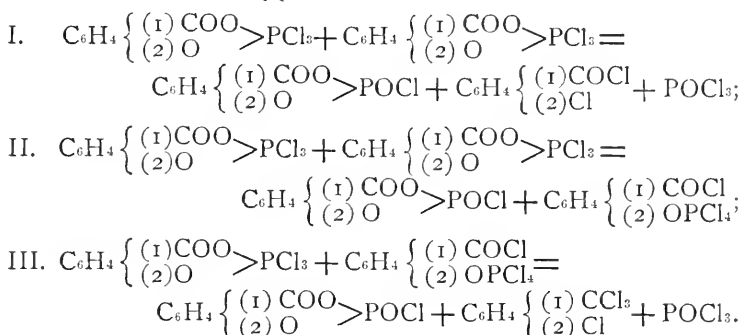
As soon as experiments (which have already been begun) have established the constitution of the three chlorides $o\text{-}C_7H_4ClPO_4$, $o\text{-}C_7H_4Cl_3PO_3$, and $o\text{-}C_7H_4Cl_5PO_2$, we shall be in a position to determine which of the above series of reactions is the correct one.

By the results above described, concerning the action of phosphorus pentachloride on salicylic acid, we have obtained, for the first time, a correct idea of the action of phosphorus pentachloride upon an aromatic mono-hydroxy-mono-carboxy-acid. For the purpose of completing the generalisation of the reaction, we have extended it to the two isomers of salicylic acid—the meta- and para-hydroxy-benzoic acids.

THE ACTION OF PHOSPHORUS PENTACHLORIDE UPON META-HYDROXY-BENZOIC ACID.

Action of one molecule of phosphorus pentachloride on meta-hydroxy-benzoic acid. Formation of the chloride,
$$C_6H_4 \begin{cases} (1)\ COCl \\ (3)\ OPOCl_2 \end{cases}.$$
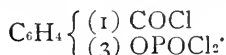
Perfectly pure, dry meta-hydroxy-benzoic acid was mixed in a

flask with a little more than one equivalent of phosphorus penta-
chloride. Both substances dissolved slowly with evolution of
hydrochloric acid, and constituted finally a clear yellow liquid.
This, after warming a few minutes at 100° to expel the last traces
of hydrochloric acid, was immediately rectified in a vacuum. At
first a small quantity of phosphorus oxychloride mixed with penta-
chloride came over, then the temperature rose rapidly, and between
160° and 180°, under 11-12 mm. pressure, a colorless liquid dis-
tilled over. Upon being again distilled, this product boiled
between 168° and 170° under 11 to 12 mm. pressure. The analyt-
ical results led to the formula $C_7H_4Cl_3PO_3 \left(= C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (3)\ OPOCl_2 \end{Bmatrix} \right)$.

The specific gravity, determined by means of a Sprengel's
U-shaped pyknometer, is $d^{20}_4 = 1.54844$.

The chloride, m-$C_7H_4Cl_3PO_3$, thus formed is therefore isomeric
with the compound obtained by the action of phosphorus penta-
chloride on salicylic acid. While, however, for the latter, both of the
formulas $C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (2)\ OPOCl_2 \end{Bmatrix}$ and $C_6H_4 \begin{Bmatrix} (1)\ COO \\ (2)\ O \end{Bmatrix} > PCl_3$ are
worthy of consideration, in the case of the meta-chloride the second
formula is highly improbable, as in the case of meta-compounds in
general, experience has shown that the chains in the meta-position
do not condense to form closed rings. We prefer, therefore, for this
first product of the action of phosphorus pentachloride on meta-
hydroxy-benzoic acid the formula $C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (3)\ OPOCl_2 \end{Bmatrix}$.

The reaction would then be as follows:

$$C_6H_4 \begin{Bmatrix} (1)\ COOH \\ (3)\ OH \end{Bmatrix} + PCl_5 = C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (3)\ OH \end{Bmatrix} + POCl_3 + HCl\ ;$$

$$C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (3)\ OH \end{Bmatrix} + POCl_3 = C_6H_4 \begin{Bmatrix} (1)\ COCl \\ (3)\ OPOCl_2 \end{Bmatrix} + HCl.$$
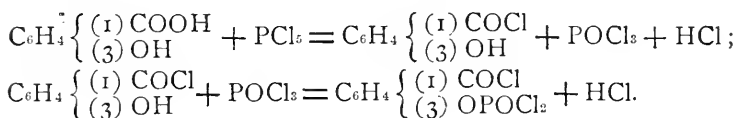
Treated with water, the chloride dissolved slowly under evolu-
tion of heat and hydrochloric acid. From this solution crystallised,
on cooling, fine white leaflets of a substance extremely soluble in
water, alcohol and ether. On recrystallising from alcohol, this
product melted at 200°–201°, and the analyses led to the formula

$$C_7H_7PO_6 \left(= C_6H_4 \begin{Bmatrix} (1)\ COOH \\ (3)\ OPO_3H_2 \end{Bmatrix} \right).$$

From its formation, and from the results obtained by the an-

alyses, we may designate this body as meta-carboxyl-phenyl-ortho-phosphoric acid. Its formation is explained by the reaction:

$$C_6H_4 \left\{ \begin{array}{l} (1)\ COCl \\ (3)\ OPOCl_2 \end{array} \right. + 3H_2O = C_6H_4 \left\{ \begin{array}{l} (1)\ COOH \\ (3)\ OPO(OH)_2 \end{array} \right. + 3HCl.$$
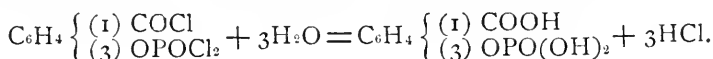
Decomposition of the meta-chlorcarbonyl-phenyl-orthophosphoric dichloride by distillation under ordinary pressure.

About thirty grams of pure chloride were heated on a graphite bath. The temperature rose slowly, until between 315° and 322° a colorless mobile liquid, smelling strongly of phosphorus oxychloride, distilled over, the residue in the retort forming a thick black substance, which when warm was liquid, but upon cooling became quite solid.

The distillate was immediately rectified under ordinary pressure. The larger part thereof boiled between 108° and 112°, and from this, as well as from its other properties, was easily recognised as phosphorus oxychloride. As soon as this fraction had distilled over, the temperature rose rapidly, and the remaining substance came over between 300° and 310°, no residue of any consequence being left. This second fraction was then rectified under diminished pressure, and boiled between 165° and 175° under a pressure of 13-14 mm. Decomposed with water, it gave hydrochloric acid and a precipitate of white leaflets melting between 200° and 201°, which, on analysis, proved to be meta-carboxyl-phenyl-orthophosphoric acid.

Although the formation of phosphorus oxychloride during the distillation under ordinary pressure would seem to indicate that a decomposition of the original chloride had taken place, we were nevertheless unable to isolate from the decomposition product any meta-chlor-benzoyl chloride. The boiling point of the second fraction, and its behavior with water, proved conclusively that it consisted essentially of unchanged chloride. From the residue, which it was not possible to distill further, we recovered, by means of water or alkali, only meta-hydroxy-benzoic acid.

The most important result of these experiments in decomposing the meta-chloride is evidently this: the phenol-oxygen atom which is in the *meta*-position is by no means so easily replaced by chlorine as the phenol-oxygen atom which occupies the corresponding position in the *ortho*-compound.

The action of a second molecule of phosphorus pentachloride on meta-chlor-carbonyl-phenyl-orthophosphoric dichloride. Formation of the chloride m-$C_7H_4Cl_5PO_2$.

The reaction was carried out in a manner exactly analogous to that described under the corresponding ortho-compound, rather more than equal molecules of each substance being employed, in order to insure a better yield of product. After heating the tubes for about thirty hours, the phosphorus pentachloride dissolved completely, and the product consisted a clear yellow liquid. On opening the tubes, no pressure of any consequence was manifested. On rectifying under diminished pressure, we obtained as the first fraction a large amount of phosphorus oxychloride mixed with more or less pentachloride. A small amount of unchanged chloride came over between 160° and 175° under 11 mm., but the chief product boiled between 176° and 179°, the pressure remaining the same. The residue consisted of a relatively small amount of a yellowish syrup which could not be distilled further.

Analyses of a portion boiling at 178° under 11 mm. pressure gave results in accordance with the formula $C_7H_4Cl_5PO_2$, and the compound is evidently analogous to that obtained under similar conditions from salicylic acid. For this latter we have already suggested two formulas, $C_6H_4\left\{\begin{array}{l}(1)\ CCl_3\\(2)\ OPOCl_2\end{array}\right.$ and $C_6H_4\left\{\begin{array}{l}(1)\ COCl\\(2)\ OPCl_4\end{array}\right.$

Under the assumption that ortho-oxybenzo-trichloride (which is as yet unknown) is easily converted by water into salicylic acid, we may explain the behavior of the chloride o-$C_7H_4Cl_5PO_2$ with water on the basis of the first constitutional formula. Although this assumption in the case of the ortho-oxybenzo-trichloride seems, to a certain degree, justifiable, there is, nevertheless, no reason for the supposition that the meta-oxybenzo-trichloride (also unknown) acts in the same manner. Consequently we expected that the chloride m-$C_7H_4Cl_5PO_2$, by treatment with water, would go over into the acid $C_6H_4\left\{\begin{array}{l}(1)\ CCl_3\\(3)\ OPO(OH)_2\end{array}\right.$ if its constitutional formula was $C_6H_4\left\{\begin{array}{l}(1)\ CCl_3\\(3)\ OPOCl_2\end{array}\right.$ As a matter of fact, however, on being brought together with water, all the chlorine was eliminated, and, with a violent effervescence of hydrochloric acid, a crystalline compound—the above-described m-carboxyl-phenyl-orthophosphoric acid—was formed :

$$m\text{-}C_7H_4Cl_5PO_2 + 4H_2O = C_6H_4 \begin{Bmatrix} (1) & COOH \\ (3) & OPO(OH)_2 \end{Bmatrix} + 5HCl.$$

After being once recrystallised from water, this compound melted at 200°–201°.

This direct formation of *m*-carboxy-phenyl-orthophosphoric acid by the action of cold water on the chloride $m\text{-}C_7H_4Cl_5PO_2$, we consider a valuable argument for the formula $C_6H_4 \begin{Bmatrix} (1) & COCl \\ (3) & OPCl_4 \end{Bmatrix}$, for which we hope to be able to furnish later direct experimental proof.

The action of a third molecule of phosphorus pentachloride upon the chloride m-C₇H₄Cl₅PO₂. Formation of meta-chlor-benzo-trichloride.

The action of a third molecule of phosphorus pentachloride upon the chloride $m\text{-}C_7H_4Cl_5PO_2$. *Formation of meta-chlor-benzo-trichloride.*

The reaction was carried out in a manner quite analogous to that employed in the case of the corresponding ortho-compound. A slight excess of phosphorus pentachloride was used, and after three days' heating at 170°–180° all had dissolved, and the contents of the tubes consisted of a clear yellowish liquid. No pressure of any consequence was observed when the tubes were opened. Rectified under diminished pressure, the following products were obtained. First, a large quantity of phosphorus oxychloride, mixed with more or less pentachloride, came over, then the greater part of what remained in the retort between 123° and 137° under 14–15 mm. pressure. A relatively small portion, undoubtedly unchanged chloride and boiling at 175°–180°, formed the last fraction. No residue worth mentioning remained in the retort.

The second fraction was immediately rectified under ordinary pressure, and showed the boiling point 247° to 250°, no residue remaining. An analysis showed that it was almost pure meta-chlorbenzo-trichloride.

From this we may reasonably conclude that phosphorus pentachloride reacts upon meta-trichlor-methyl-phenyl-ortho-phosphoric dichloride exactly as upon the corresponding ortho-compound, the equation being

$$C_6H_4 \begin{Bmatrix} (1) & CCl_3 \\ (3) & OPOCl_2 \end{Bmatrix} + PCl_5 = C_6H_4 \begin{Bmatrix} (1) & CCl_3 \\ (3) & Cl \end{Bmatrix} + 2POCl_3.$$
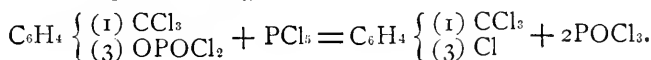
THE ACTION OF PHOSPHORUS PENTACHLORIDE UPON PARA-HYDROXYBENZOIC ACID.

Action of the first molecule, forming the chloride

$$C_6H_4 \begin{cases} (1)\ COCl \\ (4)\ OPOCl_2 \end{cases}.$$
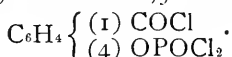
Para-hydroxybenzoic acid crystallises with one molecule of water, which must be removed by heating at 100° before the phosphorus pentachloride can be added. The dry acid and phosphorus pentachloride on being brought together enter into reaction much more violently than either salicylic or meta-hydroxybenzoic acid. Hydrochloric acid is given off rapidly, and the temperature rises so high that in cases where more than 10 or 15 grams of acid are employed, it is advisable to cool the mixture. The raw product consists of a clear yellowish liquid which, on being distilled under diminished pressure, yields as the first fraction phosphorus oxychloride and pentachloride. The temperature then rises rapidly to about 165°, and the greater part of the remaining substance distills over between 165° and 170° under 12 mm. pressure. The residue, a relatively small portion only of the original contents of the retort, is a thick dark syrup from which, by boiling with water, para-oxybenzoic acid is easily recovered.

The analyses led to the formula

$$C_7H_4Cl_3PO_3 \left(= C_6H_4 \begin{cases} (1)\ COCl \\ (4)\ OPOCl_2 \end{cases} \right).$$

The specific gravity of the compound is $d^{20}_{4} = 1.54219$.

According to its constitution we may designate it as *para-chlorcarbonyl-phenyl-orthophosphoric dichloride*, the reactions by which it is formed being:

$$C_6H_4 \begin{cases} (1)\ COOH \\ (4)\ OH \end{cases} + PCl_5 = C_6H_4 \begin{cases} (1)\ COCl \\ (4)\ OH \end{cases} + POCl_3 + HCl;$$

$$C_6H_4 \begin{cases} (1)\ COCl \\ (4)\ OH \end{cases} + POCl_3 = C_6H_4 \begin{cases} (1)\ COCl \\ (4)\ OPOCl_2 \end{cases} + HCl.$$
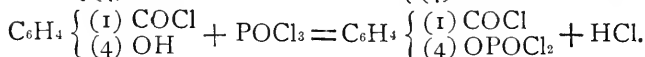
As in the case of salicylic and meta-hydroxybenzoic acids, a much better yield of the chloride is obtained by using an excess of phosphorus pentachloride.

This chloride, if treated with water, behaves quite like the meta-compound. Hydrochloric acid is given off, and the residual liquid deposits, on cooling, a heavy precipitate of white leaflets melting at 200° and very easily soluble in water, alcohol and ether.

An analysis proved it to be *para-carboxyl-phenyl-orthophosphoric acid*, $C_6H_4 \begin{cases} (1) \text{ COOH} \\ (4) \text{ OPO(OH)}_2 \end{cases}$. It is formed according to the following reaction:

$$C_6H_4 \begin{cases} (1) \text{ COCl} \\ (4) \text{ OPOCl}_2 \end{cases} + 3H_2O = C_6H_4 \begin{cases} (1) \text{ COOH} \\ (4) \text{ OPO(OH)}_2 \end{cases} + 3HCl.$$
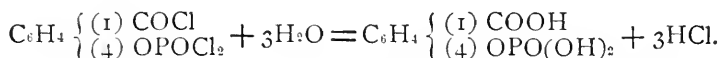
As in the case of the corresponding meta-compound, the para-carboxyl-phenyl-orthophosphoric acid is very stable. Neither compound gives up its phosphoric acid even by boiling with potash. The para-compound, however, may be broken up into para-hydroxybenzoic acid and phosphoric acid by heating with water for several hours at 150°–160° in a sealed tube.

Decomposition of the chloride $C_6H_4 \begin{cases} (1) \text{ COCl} \\ (4) \text{ OPOCl}_2 \end{cases}$ *by slow distillation under ordinary pressure.*—20 grams of pure chloride were heated on a graphite bath just as in the case of the meta-chloride. The temperature, measured by a thermometer dipping below the surface of the liquid in the flask, rose rapidly, and between 325° and 330° a clear colorless fluid began to distill over. Toward the end of the operation the residue in the boiling-flask suddenly decomposed, leaving a mass of light puffy charcoal which completely filled the apparatus.

The distillate was rectified under diminished pressure. The first fraction consisted of a small quantity of phosphor-oxychloride, the second of a few drops of a liquid boiling between 125° and 129° under 13–14 mm. pressure. The principal part came over in the third fraction, evidently unchanged chloride, boiling between 175° and 177° under 13–14 mm. pressure. The third fraction gave, moreover, with water, para-carboxyl-phenyl-orthophosphoric acid, melting point 200°.

The second fraction, boiling point 125°–129° under 13–14 mm. pressure, was analysed and found to be almost pure para-chlorbenzoyl chloride.

The action of a second molecule of phosphorus pentachloride on the chloride $C_6H_4 \begin{cases} (1) \text{ COCl} \\ (4) \text{ OPOCl}_2 \end{cases}$.—Pure chloride was heated with rather more than one equivalent of phosphorus pentachloride in a sealed tube, at first for one day at 150°. As the phosphorus pentachloride did not dissolve under these conditions, the tempera-

ture was raised on the following day to 160°, and as this did not suffice, finally on the third day to 170°–180°. At this last temperature the phosphorus pentachloride slowly dissolved, giving a clear yellow product. The first product of the rectification of this, under diminished pressure, was phosphorus oxychloride mixed with pentachloride. Under 14 mm. pressure the second fraction came over between 117° and 129°, the third between 134° and 165°, and the last between 170° and 177°. This last portion, which consisted of but a few drops, was unchanged para-chlorcarbonyl-phenyl-orthophosphoric dichloride. On being again rectified under diminished pressure (13–14 mm.), the greater part of the second fraction came over between 108° and 112°. This gave by subsequent distillation under the same pressure, two portions, the first boiling at 108°–110°, the second at 110°–112°. Both portions were analysed, and found to be, in all probability, para-chlorbenzoyl chloride, rendered slightly impure by the presence of traces of para-chlorbenzo-trichloride. From our experience in obtaining the ortho-chlorbenzoyl chloride in the pure state we concluded that it would not be worth while to attempt to isolate the para-chlorbenzoyl chloride from the accompanying para-chlor-benzo-trichloride. Moreover, all doubts as to the nature of the substance were removed on treating it with water. We obtained with ease para-chlorbenzoic acid, melting at 236°–237°, while a very small portion, smelling quite like benzo-trichloride, was not attacked.

The third fraction, bpt. under 14 mm. 134°–165°, on being again distilled under the same pressure, showed the boiling point 125°–137°. The amount of the distillate was very small, but we succeeded in making an analysis of it and thus proving it to be nearly pure para-chlorbenzo-trichloride.

From what has been shown above it is evident that the reaction of phosphorus pentachloride upon the chloride $C_6H_4 \begin{cases} (1) \; COCl \\ (4) \; OPOCl_2 \end{cases}$ is not the same as in the case of the corresponding ortho- and meta-compounds. Upon both these last mentioned substances the first molecule reacts in such a manner that the oxygen of the group COCl is replaced by two chlorine atoms, the phenol-oxygen not being attacked. It is only by the action of a second molecule of phosphorus pentachloride that this phenol-oxygen atom is replaced by chlorine. In the case of the para-chloride, para-chlor-

benzoyl chloride is the first product, and the small amount of para-chlorbenzo-trichloride which is formed probably results from the action of phosphorus pentachloride upon it:

$$C_6H_4 \left\{ \begin{matrix} (1)\ COCl \\ (4)\ OPOCl_2 \end{matrix} \right. + PCl_5 = C_6H_4 \left\{ \begin{matrix} (1)COCl \\ (4)Cl \end{matrix} \right. + 2POCl_3 ;$$

$$C_6H_4 \left\{ \begin{matrix} (1)\ COCl \\ (4)\ Cl \end{matrix} \right. + PCl_5 = C_6H_4 \left\{ \begin{matrix} (1)\ CCl_3 \\ (4)\ Cl \end{matrix} \right. + POCl_3.$$
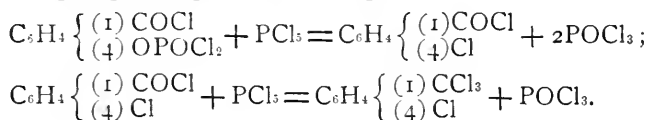
In the course of the foregoing we have referred several times on the one hand to the similarity, on the other to the characteristic differences which the three isomeric mono-hydroxybenzoic acids exhibit when brought into reaction with phosphorus pentachloride. Deeming it superfluous to repeat these remarks here, we would say, in conclusion, that investigations have already been undertaken in this laboratory with a view of extending this reaction to other suitable hydroxy acids of the fatty series.

Bonn, *April*, 1887.

THE ATOMIC WEIGHT OF ZINC AS DETERMINED BY THE COMPOSITION OF THE OXIDE.

By H. N. Morse and W. M. Burton.

About five years ago one of us, with Dr. E. H. Keiser, began a series of experiments upon the preparation of pure zinc, the object in view being a redetermination of the atomic weight of that element with the metal as a starting point. Other methods of preparation having proved more or less unsatisfactory, we determined to attempt the fractional distillation of the metal in a vacuum. We were not then aware of the work of A. Schuller[1] or of E. Demarçay[2] upon the distillation of substances in a vacuum. Having found by preliminary experiments made with the ordinary commercial zinc that the method was likely to prove very effective for the separation of the metal from the impurities which are usually associated with it, especially lead, we provided ourselves with a supply of the material which Dr. Schuchardt, of Goerlitz, designated in his catalogue of chemicals as " Zincum met. absolut. chem. pur. (für

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[1] Jahresb. 1884, 1550.   [2] Jahresb. 1882, 161.

forensische Zwecke)." This was found to contain a small amount of lead and a trace of cadmium, but no other impurities. From it the pure zinc employed in our determinations has been prepared. After Dr. Keiser's removal to Bryn Mawr, the work was continued with the assistance of Dr. C. Piggot, who distilled the metal, analysed the various fractions, and also made some preliminary practice determinations of the atomic weight. The authors of this paper are much indebted to both of these gentlemen, since the experience gained while they were associated with the work, and the suggestions offered by them, have enabled us to quickly bring the method into its present simple and satisfactory form for the final determinations.

The method adopted consists in the conversion of the zinc into nitrate, the evaporation of the excess of nitric acid, and the partial decomposition of the nitrate in a hot-air bath, and, finally, the ignition of the oxide to constant weight in a muffle. The simplicity and directness of the method are strong points in its favor, and we believe we have demonstrated beyond a reasonable doubt that the objections to it offered by Marignac[1] are founded on misapprehensions.

I.— *The Preparation of Pure Zinc.*

The distillation of the zinc was effected in hard glass tubes of the size of those ordinarily employed in the combustion of carbon compounds. Fig. 1 represents their form when ready

FIG. 1.
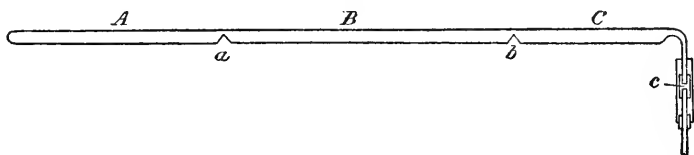
for distillation. A tube about 650 mm. in length was fused together at one end, and from 150 to 170 grams of zinc introduced. At two points, a and b, the glass was softened in the flame of the blast lamp, and depressed by means of a red-hot file, thus dividing the tube into three compartments which we designate as A, B and C. The open end of the tube was then drawn out and turned

[1] Archives des Sciences Phys. et Nat. (3) **10,** 194.

down in the manner indicated. At *c* it was connected with a Sprengel air pump having a manometer attached. The attachment of the tube to the pump was made by means of rubber tubing firmly tied with waxed shoemaker's thread, and surrounded by mercury. The outside of the rubber connecting tube was washed with a solution of mercuric chloride in order to bring about a closer adhesion of the mercury. The use of glycerin joints was found to be impracticable because of the action of the vapor of zinc upon that of glycerin, by which the oxide of zinc was formed, and volatile substances were liberated whose presence rendered a high degree of exhaustion impossible.

The tube having been thoroughly exhausted was then heated in a combustion furnace throughout nearly its whole length, but most strongly in the compartment *A* containing the zinc, and least strongly in the compartment *C.* When raised to its fusing point the zinc begins to distill quite rapidly from *A* into *B*, and more slowly from *B* into *C.* The vapors from *A* condensed in *B* in the form of globules upon the glass, which when they had attained sufficient size ran down upon the floor of the tube, giving when cooled a thick bar of the metal having the form of the lower half of the tube. Those globules which were left upon the upper portion of the tube when the heat was turned off solidified into beautiful but apparently very complicated crystals. When the metal in *A* had been reduced to about one fourth of the quantity originally taken, and about one tenth of the whole had distilled into *C*, the distillation was suspended. The tube usually cracked on cooling, but not until the temperature had fallen so low that there was little danger of oxidation of the zinc resulting from the admission of air. The portion remaining in *A* and that which had collected in *C* were rejected. The portion collected in *B* was four times redistilled in the manner described. The material deposited in *B* during the fifth distillation was employed for the determination of the atomic weight. It was carefully analysed, but we were unable to find in it any impurity whatever. It was also spectroscopically examined by Mr. J. S. Ames, Fellow in Physics in this university. The following is a copy of his written report:

" I have examined spectroscopically three specimens of the zinc prepared by distillation in a vacuum. The apparatus used was Prof. Rowland's induction coil, driven by a Siemens alternating dynamo, and his 20-foot concave grating spectroscope. Photo-

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graphs were taken in the ultra violet from w. l. 4000 to w. l.
2000, with wide slit and unusually long exposures.   In this region
are many of the strongest lines of such metals as lead, cadmium,
tin and indium ; and in a specimen of so called C. P. zinc several
lines belonging to each of these metals were found on the nega-
tives. With the zinc prepared by distillation in a vacuum, however,
not a trace of any of the above impurities could be found."

The rejected portions in *A* and *C* were also analysed, but we
were not able to find any impurities in them, except after the first
distillation, when the contents of *A* were found to contain a small
amount of lead, and those of *C* a trace of cadmium.

II.— *The Preparation of Pure Nitric Acid.*

It was found impossible by distilling from a platinum retort to
prepare an acid which on evaporation would not leave a residue.
The distillate contained in every case a small quantity of gold
which the acid had extracted from the solder used in joining the
tube to the body of the retort.   We therefore made use of the
following simple arrangement, Fig. 2.   Two platinum dishes, one

FIG. 2.
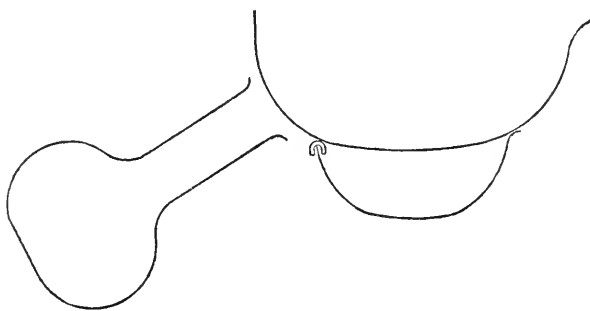
100 mm., the other 70 mm. wide, were arranged as shown in the
figure, the two being kept apart by hooks of thick platinum wire
hung over the edge of the lower one.   The upper one was cooled
by putting into it pieces of ice.   The acid, having first been treated
with nitrate of silver, was then slowly distilled from a small flask
so placed that the vapors issuing from it would strike against and
condense upon the cold surface of the upper dish.   The acid thus
obtained left no residue on evaporation.   It was preserved by

placing the smaller dish in which it was collected under a bell jar. To transfer it from the dish to the crucible in which the zinc was to be dissolved, a platinum spoon was used.

III.—*The Arrangement of Crucibles.*

Fig. 3 exhibits the arrangement of porcelain crucibles employed for the conversion of the metal into oxide. 1 is a small crucible

FIG. 3.
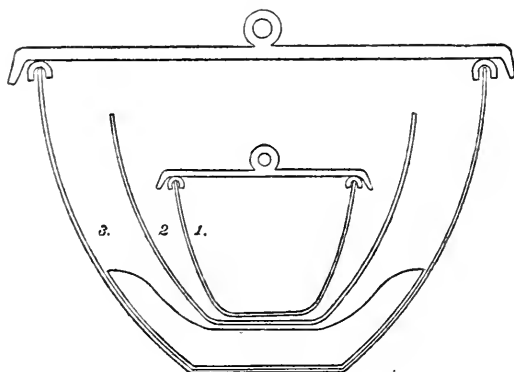
(No. 00) with lid, in which the zinc is treated with nitric acid, and the nitrate converted into oxide. The crucible and its lid are separated by means of hooks of platinum wire hung over the edge. This is necessary, in order that the vapors of nitric acid and of the oxides of nitrogen may freely escape, and that there may be free diffusion between the inside and the outside. As the temperature to which the oxide is heated in the muffle is very high—as high, at least, as that required for the fusion of steel, and far above that at which the glaze upon porcelain ware begins to soften, it is necessary to remove the glaze from the under side of the crucible lid; otherwise the lid would be found to be firmly stuck to the platinum hooks which separate it from the crucible. This removal is easily effected by means of hydrofluoric acid. 2 is a larger crucible (No. II) without lid, from the outside of which the glaze has also been removed to prevent sticking. 1 and 2 are weighed together, and not separated from the beginning to the end of the determination.

A piece of zinc weighing about one gram was broken off by

wrapping the larger piece in filter paper, placing it in a vise and prying with a pair of gas-pipe tongs. In this way a fragment was obtained which was wholly uncontaminated by the iron of the tools used. The outside was then removed by filing and washing with absolute ether.

The pair of crucibles 1 and 2 having been weighed, the zinc was placed in 1 and treated with an excess of nitric acid. When the metal had completely disappeared the pair was placed in a hot-air bath consisting of a large porcelain and a larger iron crucible, the space between them being filled with sand. This bath was then heated, very gently at first, afterwards more strongly, until the vapors of nitric acid and the oxides of nitrogen ceased to come off. From this bath 1 and 2 were transferred to crucible 3 (No. IV) (Fig. 3). The crucible 3 has in it a carefully fitted scorifier on which No. 2 rests. It is also supplied with a lid which is somewhat raised by means of hooks of platinum wire. To prevent sticking, the glaze is removed from the under side of the lid.

Finally, the whole arrangement, consisting of crucibles 1, 2 and 3, was placed in a muffle and heated for three hours to a temperature as high as that required for the fusion of steel. After weighing the oxide was again heated as before, but in no case was there any loss in weight after the first ignition.

IV.— *The Weighing.*

The balance used was a No. 8 long armed one made by Becker & Sons. It was supported by iron brackets fastened to one of the foundation walls of the laboratory. The following table gives the displacements of the zero point produced by one milligram:

Load.	No. Divisions on Scale.
Empty.	5.18
5 grams.	5.09
10	5.08
15	5.07
20	5.07
25	5.05
30	5.02
35	5.00
40	4.89
45	4.90
50	4.85

All weighings were made late at night, after the laboratory and the streets in its vicinity had become quiet. To determine whether the balance was sufficiently at rest for weighing, a thin glass bottle partly filled with mercury was kept in the case. In this way the slightest tremor could be detected by the agitation of the surface of the mercury. The methods of weighing by vibrations and of double weighing—that is, upon both pans—were employed throughout. Each zero point was determined by means of three series of observations, one with short, another with long, and a third with medium excursions of the pointer. The weight producing a given displacement of the zero point was not calculated from the above table of sensibility. The sensibility of the balance with the load, whatever it might be, was determined at the time of weighing, and from that the weight to be ascertained was estimated. In order to assure himself that the weighings should not be vitiated by changes in the relative lengths of the arms, the operator—having some hours beforehand closed the room, shut off the register through which the room was warmed, and lighted the lamp, which was stationed above and behind his head—would determine the position of the zero point of the empty balance. After waiting an hour, without moving from his place before the balance, he would again determine the zero point. For the same purpose the zero point was always determined just before and just after each weighing. This method is believed to be much more certain than that of placing thermometers at each end of the balance case.

The weights used belonged to a set obtained from Becker Brothers. At our request they were adjusted with the utmost care by the makers, and on comparison they showed unusually good agreement.

In order to avoid the necessity of reducing our weighings, and to make ourselves at the same time independent of the varying humidity of the atmosphere, the crucibles 1 and 2 were weighed by taring. Two crucibles of the same size, and as nearly as possible of the same weight, but slightly lighter, were selected and prepared in every respect like 1 and 2 to serve as a tare. The platinum hooks upon 1, and those upon the corresponding crucible of the tare, were brought to the same weight by filing. The weight of the tare was then brought to within less than a milligram of that of the crucibles 1 and 2 by the addition of a thin piece of porcelain obtained from a crucible of the same kind. The slight

Morse and Burton.

difference between the weight of the crucibles and that of the tare could then be determined by the displacement of the zero point without the use of weights. The tares were treated with nitric acid and heated in the bath and muffle in every respect like the crucibles in which the determinations were made.

V.— *The Results.*

The method in its perfected form worked so smoothly that we were not obliged to discard a single determination. The following table contains the results of fifteen successive experiments:

	Wt. of Zinc.	Wt. of ZnO.	At. Wt. Zn. (O = 16).	At. Wt. Zn. (O = 15.96).
1	1.11616	1.38972	65.281	65.119
2	1.03423	1.28782	65.253	65.091
3	1.11628	1.38987	65.281	65.119
4	1.05760	1.31681	65.281	65.118
5	1.04801	1.30492	65.268	65.105
6	1.02957	1.28193	65.276	65.113
7	1.09181	1.35944	65.273	65.110
8	1.16413	1.44955	65.258	65.095
9	1.07814	1.34248	65.258	65.095
10	1.12754	1.40400	65.256	65.093
11	.91112	1.13446	65.272	65.109
12	1.10011	1.36981	65.264	65.101
13	1.17038	1.45726	65.273	65.111
14	1.03148	1.28436	65.263	65.100
15	1.05505	1.31365	65.277	65.114
		Mean,	65.269	65.106
		Highest,	65.281	65.119
		Lowest,	65.253	65.091
		Difference,	.028	.028

If we calculate the atomic weight from the sums of the quantities of zinc taken and oxide obtained, as recommended by Meyer and Seubert,[1] we have:

Atomic Wt. of Zn (O = 16).	Atomic Wt. of Zn (O = 15.96).
65.2693	65.1066

[1] Die Atomgewichte der Elemente, p. 13.

We give below the two series of results obtained by Marignac[1] by the analysis of the double chloride of zinc and potassium $(O = 16)$:

	1st Series.			2d Series.
	65.26			65.28
	65.22			65.39
	65.37			65.32
	65.31			
	65.28		Mean,	65.33
			Highest,	65.39
Mean,	65.29		Lowest,	65.28
Highest,	65.37		Difference,	0.11
Lowest,	65.22			
Difference,	0.15			

VI.—*Objections to the Method.*

Marignac[2] has offered two objections to this method of determining the atomic weight of zinc which, if well founded, would render the results obtained by it wholly worthless; we have therefore taken great pains to investigate their validity.

These objections are:

1st. That the oxide of zinc dissociates at high temperatures.

2d. That the oxide of zinc, though heated to the temperature at which it begins to dissociate, still retains oxides of nitrogen.

To determine whether the oxide of zinc does dissociate at high temperatures, we divided about fifteen grams of the oxide, prepared from our pure metal, nearly equally between two platinum crucibles which had been tared by other crucibles of the same kind. The crucibles containing the oxide, and the tares belonging to them, were then heated for three hours in a muffle furnace to a temperature sufficient to fuse completely a ten gram piece of steel file which was placed upon a scorifier beside them. The difference between the weights of the crucibles plus the oxide and those of their tares was then determined. Afterwards the crucibles and tares were five times reheated the same length of time and as nearly as possible to the same temperature; in every case the piece of steel file placed in the muffle was fused. We give the results in tabular form.

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[1] Archives des Sciences Phys. et Nat. (3) **10**, 204.　　　　[2] Ibid. **10**, 194.

SERIES I.

	Apparent Gain.	Apparent Loss.
After 1st ignition,	0.00004 gram.	...
After 2d,	0.00002	...
After 3d,	...	0.00005 gram.
After 4th,	0.00004	...
After 5th,	...	0.00004

Total gain, 0.0001.   Total loss, 0.00009

SERIES II.

	Apparent Gain.	Apparent Loss.
After 1st ignition,	0.00006 gram.	...
After 2d,	...	0.00005 gram.
After 3d,	...	0.00001
After 4th,	0.00004	...
After 5th,	...	0.00001

Total gain, 0.0001.   Total loss, 0.00007

It appears from these results that the oxide of zinc does not dissociate at the fusing point of steel. The interior of the platinum crucibles in which the oxide was heated did not exhibit a trace of the tarnish observed by Erdmann.[1] The apparent gain in weight of one one-hundredth of one milligram in one case, and the apparent loss of three one-hundredths of a milligram in the other, have, of course, no significance whatever.

It remained for us to find the cause of the tarnish observed by Erdmann, and of the undoubted loss of weight observed by Marignac,[2] when the oxide of zinc is heated in a platinum crucible over a flame. This we have done. In a former article[3] we have shown that the atmosphere within any platinum vessel heated by a flame receives free hydrogen, and that the phenomenon referred to is in all probability one of reduction, and not of dissociation as Marignac supposed. In that article we suggested that perhaps the platinum itself may be a cause of the dissociation of water in the flame, but more recent experiments have convinced us that this decomposition is quite independent of the presence of the platinum.

To test for the presence of the oxides of nitrogen, Marignac[4] dissolved the oxide of zinc in hydrochloric acid in the presence of

[1] Pogg. Ann. **62**, 612.
[3] This Journal **10**, 148.
[2] Archives des Sciences Phys. et Nat. (3) **10**, 195.
[4] Archives des Sciences Phys. et Nat. (3) **10**, 195.

starch and iodide of potassium. A slight blue coloration was observed. In order that this test may be relied upon, certain conditions must be fulfilled.

1st. The hydrochloric acid must be free from chlorine or any other oxidising agents.

2d. The iodide must be free from the iodate of potassium.

3d. All of the solutions must be free from absorbed oxygen.

4th. The solutions must be protected from the air.

Whether Marignac observed all of these precautions does not appear from his paper. Apparently he must have neglected some one or more of them, since we were not able with any specimen of our oxide to obtain the slightest trace of a blue coloration by this method.

To remove any chlorine contained in our hydrochloric acid we agitated the diluted acid with metallic mercury. To remove the iodate from the iodide of potassium we boiled the solution with zinc amalgam.

To remove absorbed oxygen, all of our solutions were thoroughly boiled. The order in which the materials were brought together is as follows : The boiling solution of iodide was poured into the boiling starch paste in an Erlenmeyer flask. To this mixture was added first the zinc oxide and then the boiling hydrochloric acid. The steam rising from the liquid sufficed to protect it from the air.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

THE REMOVAL OF IODATE FROM THE IODIDE OF POTASSIUM BY MEANS OF ZINC AMALGAM.

BY H. N. MORSE AND W. M. BURTON.

The frequent occurrence of the iodate of potassium in the commercial iodide, and the difficulty of removing it, are two of the most serious obstacles in the way of the free use of the iodometric method, either for quantitative work, or for the detection of oxidising agents. The fact that so many methods have been

proposed for the preparation of iodide free from the iodate, and for the removal of the latter from the former, indicates that a simple and effective method for the preparation of the pure iodide of potassium is much needed, but not readily found.

In the course of our work upon the atomic weight of zinc it became necessary for us to prepare some iodide of potassium free from iodate, in order to test for the presence of the oxides of nitrogen, which Marignac[1] supposes to remain in the oxide of zinc prepared from the nitrate, even up to the dissociating temperature of the oxide. The method which we employed for the purpose consists in boiling the solution of the iodide with zinc amalgam. By this means the iodate is completely reduced with formation of zinc hydroxide, and the filtered solution is found to be free from both mercury and zinc. It is recommended to make the amalgam quite rich in zinc, and to have the filter paper, through which the hot solution of iodide is to be filtered, saturated with boiling water. The efficacy of the method was tested upon solutions of pure iodate of potassium. In one case one gram of the iodate dissolved in 50 cubic centimeters of water was completely reduced within forty-five minutes; in another, two grams dissolved in the same amount of water were reduced within one hour and a quarter. The bromate and chlorate of potassium are also reduced by zinc amalgam, but much more slowly than the iodate. Of the two, the chlorate reduces less rapidly than the bromate.

The zinc amalgam used in the reduction is best prepared by agitating zinc dust with mercury in the presence of tartaric acid and washing with water.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

A METHOD FOR THE ANALYSIS OF BUTTER, OLEOMARGARINE, ETC.

BY H. N. MORSE AND W. M. BURTON.

The method which we here describe has been in use in this laboratory during the past year. Its advantages are: 1st. That it

[1] Archives des Sciences Phys. et Nat. (3) **10**, 195.

is volumetric throughout ; 2d. That it obviates the necessity of weighing the specimen of fat ; 3d. That it readily discriminates between genuine butter and any mixture of cocoanut oil and other fats or oils. That is, it succeeds at that point where the methods of Hehner and of Koettstorfer may fail.

It depends upon the fact that the relative quantities of alkali required to neutralise the soluble and insoluble acids are for any one fat or oil quite constant, but for different fats or oils quite variable.

The following statement contains the relative percentages of alkali required to neutralise the soluble and insoluble acids of butter, cocoanut oil, cottonseed oil, oleomargarine, lard, and beef tallow :

	Per cent. KOH required for insoluble acids.	Per cent. KOH required for soluble acids.
1. Butter	86.57	13.17
2. Cocoanut oil (unwashed),	91.95	8.17
3. Cocoanut oil (washed with hot water)	92.43	7.42
4. Cocoanut oil (washed with dilute Na_2CO_3) . .	92.33	7.45
5. Cottonseed oil	92.05	7.76
6. Oleomargarine	95.40	4.57
7. Lard	95.96	3.82
8. Beef tallow	96.72	3.40

There is, between the amounts of alkali required to neutralise the soluble acids of butter and of unwashed cocoanut oil, a clear difference of 5 per cent.

Evidently it would not be possible to make any mixture of the other substances than butter in this list which would not show even a greater divergence from butter in respect to the soluble acids. The only way in which the proportion of soluble acids can be increased beyond 8.17 per cent. is by the addition of butter itself.

It was found by Moore[1] that a mixture of butter 50 per cent., oleomargarine 27.5 per cent., and cocoanut oil 22.5 per cent., could not be distinguished from butter either by the method of Hehner or by that of Koettstorfer. Such a mixture gave us :

Per cent. KOH required for insoluble acids.	Per cent. KOH required for soluble acids.
90.17	9.70

[1] This Journal **6,** 418.

There is still a difference in respect to soluble acids of 3.47 per cent. between such a mixture and butter; and it would not be practicable to so far increase the proportion of butter that there would not still be a perceptible difference in this respect between genuine butter and the mixture. The figures thus far given are mean quantities; we give in the following table the individual results from which they were calculated. The first column contains the number of milligrams of potassium hydroxide required to saponify one gram of fat; the second and third columns, the number of milligrams required to neutralise the insoluble and soluble acids contained in one gram of the fat; while the fourth and fifth give the percentages corresponding to the quantities in two and three.

A. *Butter.*

	I. Mgs. KOH for 1 gram fat.	II. Mgs. KOH for insoluble acids.	III. Mgs. KOH for soluble acids.	IV. Per cent. KOH for insoluble acids.	V. Per cent. KOH for soluble acids.
1.	230.39	199.57	30.21	86.62	13.11
2.	231.14	199.83	30.94	86.45	13 38
3.	230.66	200.11	30.07	86.75	13.04
4.	230.71	199.67	30.54	86.53	13.23
5.	230.94	199.85	30.29	86.53	13.11
				Mean, 86.57	13.17

B. *Cocoanut Oil* (unwashed).

1.	266.88	245.50	21.91	91.98	8.20
2.	266.96	244.87	22.01	91.72	8.24
3.	266.58	245.68	21.53	92.15	8.07
				Mean, 91.95	8.17

Cocoanut Oil (washed with hot water).

4.	262.44	243.17	19.11	92.65	7.28
5.	263.33	242.84	19.91	92.21	7.56
				Mean, 92.43	7.42

Cocoanut Oil (washed with dilute Na_2CO_3).

1.	263.73	243.27	19.91	92.24	7.54
2.	263.42	243.39	19.31	92.39	7.33
3.	263.97	243.81	19.57	92.36	7.41
4.	264.22	243.96	19.50	92.33	7.38
5.	263.82	243.61	20.03	92.33	7.59
				Mean, 92.33	7.45

C. *Cottonseed Oil.*

1.	200.23	184.31	15.57	92.04	7.77
2.	200.54	184.04	15.71	91.77	7.83
3.	199.74	184.26	15.06	92.25	7.54
4.	199.81	183.72	15.36	91.95	7.68
5.	199.65	184.18	15.92	92.25	7.97
				Mean, 92.05	7.76

D. *Oleomargarine.*

1.	202.70	193.02	9.31	95.22	4.59
2.	202.61	193.46	9.01	95.48	4.44
3.	202.40	193.21	9.71	95.45	4.79
4.	202.62	193.65	9.21	95.57	4.54
5.	202.83	193.27	9.12	95.28	4.49
				Mean, 95.40	4.57

E. *Lard.*

1.	199.77	191.78	7.31	96.00	3.65
2.	198.93	191.11	7.91	96.06	3.98
3.	199.54	191.29	7.71	95.86	3.94
4.	199.75	191.62	7.87	95.93	3.94
5.	199.40	191.34	7.17	95.97	3.59
				Mean, 95.96	3.82

F. *Beef Tallow.*

1.	200.44	193.43	6.76	96.50	3.37
2.	199.70	193.20	6.92	96.74	3.46
3.	200.17	193.81	6.47	96.82	3.23
4.	199.60	193.13	6.91	96.76	3.46
5.	199.84	193.42	7.01	96.78	3.50
				Mean, 96.72	3.40

G.	*Mixture :*	Oleomargarine 27.5 ; Cocoanut Oil 22.5 ; Butter 50 per cent.			
1.	231.	208.77	22.65	90.37	9.81
2.	230.82	208.13	22.21	90.16	9.62
3.	231.15	208.11	22.76	90.03	9.84
4.	231.36	208.51	22.16	90.12	9.57

Mean, 90.17   9.70

Percentages for pure butter, 86.57   13.17

Difference, 3.60   3.47

The Reagents.

1. A solution of hydrochloric acid of such strength that one cubic centimeter of it is equivalent to 20 milligrams of potassium hydroxide.

2. A solution of hydrochloric acid one tenth as strong as the first.

3. A solution of potassium hydroxide in 95 per cent. alcohol approximately equivalent to the first acid.

4. A solution of potassium hydroxide in 95 per cent. alcohol one tenth as strong as the preceding.

The Mode of Procedure.

The dry and filtered fat is well stirred during solidification, to prevent the separation of the lower from the higher melting constituents.

Any convenient quantity of the material, between one and two grams, is placed in an Erlenmeyer flask having a capacity of 250 cubic centimeters, and treated with that amount of alkali which is found to be equivalent to 40 cubic centimeters of the acid No. 1. The flask is then placed upon the water-bath and heated to the boiling point of alcohol for 20 minutes.

The excess of alkali is determined by acid No. 1, with the use of phenolphthalein as the indicator. Thus the number of milligrams of KOH required for the neutralisation of all of the acids in the fat is found. The flask is then returned to the water-bath and heated until all of the alcohol has been expelled. During the evaporation of the alcohol, the soap, which in the first place was neutral, becomes alkaline, owing doubtless to the evaporation of

a small amount of volatile acids in the form of esters; but the loss from this cause is very slight.[1] When the odor of alcohol is no longer perceptible the soap is treated with that quantity of acid No. 1 which is necessary to exactly liberate all of the acids contained in it. This quantity is, of course, the difference between 40 and the number of cubic centimeters required to neutralise the excess of the alkali used in saponification. The flask is again returned to the water-bath and heated until the liquid becomes clear. But, in order to prevent loss of volatile acids, it is now supplied with a stopper carrying a glass tube about 5 millimeters in diameter and 400 millimeters in length. The upper end of the tube is bent downwards, and to it is attached a small U-tube containing a few cubic centimeters of water. The contents of the flask are filtered through double thick paper which has been wet with hot water and then washed with boiling water until the volume of the filtrate equals a liter; care being taken to wash thoroughly the flask itself. The contents of the condensing arrangement are washed into the filtrate. The funnel containing the washed insoluble acids is placed in the flask in which the saponification, etc., were effected, the paper pierced, and the contents washed through with hot 50 per cent. alcohol.

We thus have the soluble and insoluble acids separated, and it only remains to determine the amount of alkali required to neutralise each. The soluble acids can be directly determined by the weaker solution of the alkali; but to determine the insoluble acids it is better to add the quantity of alkali which was required for the total saponification, and, after warming upon the water-bath, to titrate back with the weaker acid. It will be observed that a determination of the insoluble acids alone by this method suffices to distinguish butter from other fats and mixtures, and that if these only are to be determined it is not necessary to use the condensing arrangement. Moreover, it is not necessary to know the exact strength of the solutions employed, since a knowledge of the relation of the acids to each other and to the alkalies is all that is needed to enable us to determine, in the fat, the relation of the soluble to the insoluble acids. Hence it is practicable to dispense

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[1] This loss may be made good by bringing the solution to a neutral condition by means of very dilute acetic acid. The quantity of acetic acid thus introduced is, of course, equivalent to the acid which has been lost during the evaporation of the alcohol. We are under the impression that there is no such loss of volatile acids during saponification, owing to the presence of a considerable excess of alkali.

with the use of the balance altogether. It is frequently recommended to make blank determinations, in order to control the error introduced by the action of the alkali upon the glass of the flasks. But a little reflection will convince one that this practice may itself be the cause of considerable error, inasmuch as the extent to which the glass is affected by the alkali depends upon its quality and upon the treatment to which it has previously been subjected. In order that the results of the blank may be applied to the correction of those of the determinations, it is necessary that the glass employed in the two cases should be the same in respect to composition and previous use in the laboratory. It is better, according to our experience, to discard the use of blanks and to boil out with strong alkali all flasks employed in such work. The subsequent action of dilute alkali upon glass which has been treated this way is very slight. The water and alcohol employed in making the standard solutions should of course be thoroughly boiled, and afterwards protected from the carbon dioxide of the air by keeping them in bottles or flasks which are supplied with stoppers carrying tubes filled with soda-lime. The use of blanks is then not necessary on account of any *carbonic* acid contained in the solution.

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CATALPIN: A BITTER PRINCIPLE.

By Edo Claassen.

Catalpin is contained in the bark and fruit of Catalpa bignonioides, Wal., a tree which, though not indigenous, is largely cultivated in the northern United States on account of its showy flower and handsome, bean-like fruit. To obtain the principle, the fruit, deprived of its seeds, which contain no catalpin, glucose, and but about 24 per cent. of thick yellow oil, or the bark, which is richer in catalpin than the fruit, was extracted with alcohol, the alcohol evaporated, the residue dissolved in water, lead acetate added, the filtrate mixed with baric carbonate, evaporated to a thin syrup, extracted with a mixture of ether and alcohol $(3:1)$,

the solution evaporated, the residue dissolved in water, and the solution filtered and concentrated. As the filtrate yielded no crystals, even after long standing, it was shaken with a comparatively large quantity of freshly ignited animal charcoal, which, on standing for 24 hours, extracted the bitter principle. The charcoal was filtered and thoroughly washed with water, then dried and extracted with boiling alcohol, the alcohol evaporated, the residue dissolved in water, the solution filtered, concentrated, and allowed to crystallise. Colorless crystals were obtained by recrystallisation. As the mother liquors contained a large proportion of the catalpin, they were concentrated, treated with lead subacetate, shaken with ether to remove impurities, and after dilution of the residue with water, the latter decomposed by hydric sulphide. The filtrate was, after the addition of baric carbonate, evaporated to a thin syrup, extracted with ether and alcohol (3 : 1), the ether and alcohol driven off, the residue dissolved in water, concentrated, and allowed to crystallise. The difficulty of isolating the bitter principle arises, probably, not so much from its solubility as from its slight tendency to crystallise, in consequence of which small quantities of other substances prevent its crystallisation.

Catalpin forms radial aggregates of white acicular or silky, slender, and often curved crystals. On heating, it first melts to a colorless liquid, then evolves a vapor with a peculiar odor, and is entirely consumed. It is quite soluble in cold and very soluble in hot water, easily soluble in alcohol, and only with difficulty in ether. It is insoluble in benzene, nearly insoluble in chloroform, and soluble in amyl alcohol, especially if hot. Chloroform precipitates it from its solution in amyl alcohol in very small radial aggregations, and from its solution in ethyl alcohol in radial aggregations of long tufted silky needles. It is a glucoside, and does not reduce alkaline copper solution unless it is first boiled with dilute sulphuric acid. In a solution of catalpin, tannin produces no precipitate nor turbidity, even after addition of dilute sulphuric acid ; but if this mixture is boiled, it becomes turbid on cooling. It does not act upon ammoniacal silver solution, ferric chloride, lead acetate, phosphomolybdic acid, phosphomolybdic acid and ammonia, potassium mercuric iodide, or solution of iodine in potassic iodide. It is precipitated by lead subacetate. It reduces gold chloride after standing with it several days. Concentrated

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hydrochloric acid and concentrated potassic hydrate solution dissolve it without change of color. The solution in cold concentrated nitric acid, colorless at first, soon becomes yellow, and on heating, reddish yellow. Concentrated sulphuric acid turns it dark at once, and dissolves it with a violet color. An addition of a little nitric acid changes this first to light brownish red and then reddish brown.

THE ELECTROLYTIC METHOD AS APPLIED TO IRON.

By Edgar F. Smith.

In estimating this metal by electrolysis I have employed solutions containing an excess of sodium citrate with a little free citric acid. In the first experiments I made use of ferric ammonium sulphate solutions of unknown strength. The volume of the liquid electrolysed varied from 76–150 cc. The electric current liberated 6 cc. of oxy-hydrogen gas per minute. The time required for the complete precipitation of the metal was from 4 to 8 hours ; in most cases it was finished in four hours. Some of the results are as follows :

(1) Deposit of iron + platinum dish = 68.6548 grams.
(2) Deposit of iron + platinum dish = 68.6550 grams.
(3) Deposit of iron + platinum dish = 68.6548 grams.
(4) Deposit of iron + platinum dish = 68.6554 grams.

The residual liquid in these experiments was found to contain no iron.

I next dissolved pure ferric ammonium sulphate in a definite volume of water: in 10 cc. of this solution I obtained, by the usual method of analysis, .0147 gram of metallic iron. Working under conditions similar to those mentioned above, I found:

(1) .0145 gram Fe. (2) .0145 gram Fe. (3) .0143 gram Fe. (4) .0150 gram Fe.

The deposit of (3) was not uniform ; particles became detached in the operation of washing and passed into the filtrate, giving evidences of the presence of iron upon subsequent testing. With

30 cc. of the same solution the iron deposit weighed .0448 gram instead of the theoretical .0441 gram.

Continuing the work with iron solutions in 10 cc. of which .0300 gram Fe was present ; using a sodium citrate solution, obtained by dissolving 28 grams of air-dried salt in 250 cc. water, I made the determinations as follows :

I. 5 cc. ferric ammonium sulphate (equivalent to .0150 gram Fe) and 10 cc. sodium citrate solution, with a few drops of citric acid, were diluted to 150 cc. and electrolysed with a current generating 12 cc. oxy-hydrogen gas per minute. Found .0149 gram Fe instead of .0150 gram. The current was allowed to act for six hours.

II. Same as I ; gave .0152 gram Fe.

III. Same as I and II, except that the entire volume of solution did not exceed 40 cc. The electrolysis was performed in a platinum crucible. Obtained .0151 gram Fe.

IV. 10 cc. iron solution (equivalent to .0300 gram Fe), 20 cc. sodium citrate, and some free citric acid, subjected to the action of a current producing 15 cc. oxy-hydrogen gas per minute, gave .0303 gram Fe. The volume of liquid was 100 cc. Time for precipitation four and a half hours

V. 5 cc. iron solution, treated as in I, gave .0149 gram Fe.

VI. 10 cc. iron solution, under the same conditions as IV, afforded .0304 gram Fe.

VII. 5 cc. iron solution gave .0151 gram Fe.

With a third solution of iron, containing .0210 gram Fe in 10 cc. of the same, I obtained :

(1) .0104 gram in 5 cc. (2) .0104 gram Fe in 5 cc. (3) .0206 gram Fe in 10 cc.

The total volume of liquid in each case amounted to 150 cc. The volume of sodium citrate solution (same strength as above) was increased to 30 cc. in these three determinations. The current had the same strength as before.

The iron deposit in all the experiments was compact, regular, and steel-like in appearance. It was washed with water, alcohol and ether, then dried and weighed. Several deposits were exposed for weeks to the air of the balance room without undergoing any alteration. In experiment VII considerable aluminium was present as sulphate. To two others I added a solution of titanium ; the precipitated iron was found to be entirely free of this metal. Solu-

tions of titanium alone, when treated just as the iron solutions were, gave no deposit. The above experiments were conducted in the cold. An account of the experiments made with a view of separating iron and titanium by electrolysis will be given later.

NOTES.

On the Influence of Light upon the Explosion of Nitrogen Iodide.

The statement of L. Gattermann in his recent paper (*Berichte d. deutsch. chem. Gesellsch.* **21**, 751; following up V. Meyer's paper in same vol., 26) on nitrogen chloride, that its explosive decomposition may be brought about, or its susceptibility to explosion much increased, by exposure to bright light, has recalled to my mind the fact, which did not specially impress me at the time, that I myself undoubtedly observed the same relation several years ago in the case of nitrogen iodide.

In a paper on the preparation and composition of the latter substance, published in the first number of this Journal (April, 1879), it was noted that on two occasions the product obtained with the composition NI_3 or N_2I_6 "exploded in some quantity *under water* with much violence and complete shattering of the vessel."

I remember distinctly that in one of these cases I had just carried to a window, through which the sun was shining, the beaker full of water at the bottom of which was the black sediment of iodide, and was gently stirring the liquid with a glass rod, holding the beaker up so as to look at it from below, when the rod touched the lower part of the side or the bottom of the vessel, and the explosion occurred.

In the other case the iodide was being washed with ice-cold water of ammonia, the vessel standing on a table exposed at the time to the direct rays of the sun. I do not remember with certainty what seemed to precipitate the explosion on this occasion, but I believe it was the pouring some fresh liquid, from the height of a few inches, on the black sediment of iodide which had just been partially drained by decantation.

Under ordinary circumstances nitrogen iodide, while *wet,* exhibits no extraordinary sensitiveness, and may be safely worked with, only becoming highly dangerous on drying, so that I have little doubt that bright sunlight was influential in bringing about these two explosions. J. W. MALLET.

AMERICAN

CHEMICAL JOURNAL.

THE FOUNDATIONS OF CHEMISTRY.[1]

By T. Sterry Hunt.

1. In an essay published forty years since, in September, 1848, the present writer advanced as the " basis of a true natural system of chemical classification," certain views as to elemental and polymeric types which have since played an important part in the science of chemistry. Assuming as the primal or fundamental type, hydrogen, H_2 (of which both water and ammonia were regarded as derivatives), and following the lead of Auguste Laurent, who had already, in 1846, represented alcohol and ether as derivatives of water, H_2O, in which one and two portions of hydrogen respectively are replaced by C_2H_5,[2] the hydrocarbons methane and ethane were considered as derivatives of H_2, in which one portion of hydrogen is replaced by CH_3 and C_2H_5. The relation between these hydrocarbons and hydrogen, and between the corresponding alcohols and water, was then declared to be one of homology, and these views were subsequently maintained and enforced on many occasions.[3]

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[1] Read before the National Academy of Sciences, April 17, 1888.

[2] Being H_2O_2 and C_4H_5 in the notation then in use, in which $H = 1$, $C = 6$ and $O = 8$.

[3] On Some Anomalies in the Atomic Volume of Sulphur, etc., with Remarks on Chemical Classification, American Journal of Science (Sept., 1848) **6**, 170-178; also, On Some Principles to be Considered in Chemical Classification, read before the American Association for the Advancement of Science, Philadelphia (1848). Ibid. 1849, **7**, 399; **8**, 89; (also **5**, 265; **9**, 65; **13**, 206); and further, The Theoretical Relations of Water and Hydrogen (1854), ibid. **17**, 194, and Chemical Gazette, 1854, p. 181; also, The Theory of Types in Chemistry (1861), Amer. Jour. Science **31**, 256, and Hunt's Chemical and Geological Essays (pp. 464-469).

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2. In the same essay the writer insisted on the existence of condensed or polymeric types, the pentachlorides being " referrible to a triple molecule, represented by H, while the corresponding trichlorides form a double molecule." The triple molecule was further said to be represented by the vapor of sulphur, then known only in its hexad form, S_6, the anomalous density of which, as compared with that of oxygen, was explained as the result of polymerism or condensation, while a similar condensation was suggested as probable in the case of ozone. The derivation of monobasic acids from the type of water, H_2O, and the possibility of anhydrides of these, and notably of the nitric anhydride (soon afterwards discovered by H. Deville), was also maintained in this essay ; while bibasic and tribasic acids were regarded as derived from condensed types corresponding to two and three molecules of water. Hydrogen, H_2, was then both the prototype and the homologue of the hydrocarbons and the chlorides, and water, H_2O, of alcohols, ethers, oxacids and anhydrides.

3. There were thus enunciated in this essay, in 1848, two distinct and important conceptions : (1) Hydrogen, H_2, is the primal chemical type, of which water and ammonia are derivatives, and to which both mineral and so-called organic or hydrocarbonaceous types may be referred. (2) Besides this dual or normal type, represented by H_2, there are also condensed or polymeric types, represented respectively by H_4 and by H_6, S_3, etc., the condensation being made evident by the increased density of the polymeric vapors. How the first of these conceptions, that of the typical relations of water and hydrogen, after having been maintained for some years, was at length adopted by Gerhardt, Brodie, and Williamson, in 1851–1852, is to-day a matter of history, and is set forth in the two papers of 1854 and 1861, already cited, in the latter of which will be found quoted a full recognition by Wolcott Gibbs of the writer's claims to priority. The second and not less important conception—that condensed or polymeric types, as represented by the higher metallic chlorides and the dense vapor of sulphur, remained, however, apparently unnoticed by chemists until after its restatement in 1854, when it was adopted by Ad. Wurtz.

4. Meanwhile the writer, in the essay already noticed, " On Some Principles to be Considered in Chemical Classification " (read in 1848 and published in 1849), had still further considered this con-

ception of polymerism with increase of specific gravity, which was then extended from vapors to solid species, and was illustrated by the allotropic modifications of carbon and of phosphorus. In 1853 an attempt was, moreover, made to show that the change from a gaseous to a liquid or solid species is itself subjected to the same general law of polymerism; while in 1867 it was maintained that vapors, and the liquid and solid products of their condensation, as in the case of steam, water, and ice, are to be regarded as distinct species, the latter two being polymeric or allotropic forms of water vapor; in a word, that all changes of state or condition in bodies are essentially chemical in their nature.[1] Similar views as to the chemical relations of gaseous, liquid and solid species were, thirty years later, in 1883, set forth by Prof. W. Spring, of Liège,[2] to whom my earlier discussions of the subject were unknown.

Continuing the line of inquiry thus begun, and followed at intervals during forty years, it is now proposed to consider briefly the relations of gaseous, liquid and solid species to temperature and pressure, together with the phenomena of allotropism, of specific gravity, of hardness, and of chemical indifference; all of which, as we have elsewhere maintained, are intimately related to and dependent upon the principle of condensation then enunciated.

5. All chemical change, of which this polymerism or condensation is but one manifestation, is subordinated to simple relations of weight and volume, which are most evident in the case of volatile and gaseous species. Well-defined gases, such as hydrogen, nitrogen, oxygen, carbon monoxide and methane, undergo, through a wide range of temperature, a constant regular change of volume, amounting for each degree centigrade to $\frac{1}{273}$ of their volume at $0°$. Their coefficient of expansion not being sensibly affected by considerable variations of pressure (which, according to Boyle's or Marriotte's law, the temperature being constant, causes the volume to vary inversely as the pressure), it follows that if we know the weight of a volume of such a gas at any given temperature and pressure, it is easy to calculate what its weight should be at any other temperature and any other pressure; as for example at $0°$ and

[1] Theory of Chemical Changes and Equivalent Volumes, 1853; American Journal of Science **15**, 226; L. E. and D. Philos. Magazine (4), **5**, 26; and in German translation, Chem. Centrbl. 1853, 849; also, The Objects and Methods of Mineralogy (1867), American Journal of Science **13**, 203. These two papers are reprinted in the author's Chemical Essays, 426-437 and 453-458. See also, A New Basis for Chemistry, etc., §§20-22.

[2] Sur l'élasticité parfaite des corps solides chimiquement definis. Bull. de l'Acad. Roy. de Belgique (2), **6**, No. 11.

760 mm., which are assumed as the standards in studying gases and vapors. These regular and constant variations in the weight and volume of a species under changes of temperature and pressure characterise the perfect or ideal gaseous state of matter. This is, however, known to us only within certain limits, since recent experiments have shown that the gases mentioned above are by the combined action of cold and pressure reduced to the state of liquids which, although still more or less compressible, are not subject to Boyle's law, and, moreover, often present great and rapidly increasing coefficients of expansion by heat; a point especially noticeable in liquids as they approach the critical point beyond which they pass, under great pressure, into dense vapors.

6. The ideal liquid, like the ideal gas, has a regular rate of thermic expansion, the coefficient of which, however, varies for the different species, and is apparently (like its compressibility) closely connected with the degree of condensation; that is to say with the interval by which it is removed from the normal gaseous species with which it is connected through dense vapors of higher integral weight. Water and mercury are, within considerable ranges of temperature, nearly ideal liquids. The ideal solid is, like the ideal liquid, permanent through considerable ranges of temperature, within which it has a regular coefficient of expansion of heat. It is sometimes more and sometimes less condensed than the corresponding liquid species; thus ice is considerably lighter than water, and solid bismuth is lighter than the fused metal, while in the greater number of cases the solid is heavier than the corresponding liquid species. For such liquids as become denser in solidification, it is well known that pressure augments their temperature of fusion. Amagat, in accordance with this principle, has reversed the well known experiment of liquefying ice by pressure, and has effected the solidification of carbon dichloride (hitherto known only in a liquid form) by a pressure of 900 atmospheres at 10°; while benzene, which under standard pressure crystallises only at 0°, is solidified at 22° under 700 atmospheres. There is probably, however, according to Amagat, "a temperature above which solidification cannot be effected by any pressure, that is to say, a critical point of solidification, as there is apparently a temperature below which the body remains solid under the feeblest pressure."[1]

On the other hand, it appears from many experiments that, in

[1] Comptes Rendus de l'Acad. des Sciences, July 18, 1887.

the language of W. Allen Miller, " there exists for every liquid a temperature at which no amount of pressure is sufficient to retain it in liquid form."[1] In other words, all such liquids and solid species, if stable—that is, not thereby undergoing heterogeneous dissociation—when heated under sufficient pressure to a temperature which for each is called its critical point, pass, with a comparatively small augmentation of volume, into the condition of very dense vapor or gas. The distinction between liquid and gas just above the critical point is, according to Andrews, impossible, and, in the language of Ramsay and Young, " would also disappear below the critical point, were it possible to follow the continuous change from liquid to gas."[2] In fact, the passage from the perfect or ideal gas proceeds through successively denser unstable polymeric gaseous or vaporous species, often more or less intermingled with one another, and perhaps also through unstable liquid species, into the ideal liquid or the ideal solid species.

7. We assume for the unit of volume in chemistry 1000 cubic centimeters or one liter, and for the unit of weight that of this volume of hydrogen at 0° and 760 mm., which equals very nearly 0.0896 gram, or, according to the determination of Regnault in the latitude of Paris, 0.089578 gram. In hydrogen, which through a wide range of temperature and pressure retains the properties of a perfect or ideal gas, we have a standard of weight upon which is built the stochiometry of modern chemistry. The weight of this volume of hydrogen at the temperature and pressure named being taken as unity ($H = 1$), that of a like volume of oxygen gas under the same conditions is approximately 16, or, more nearly, 15.96; that of nitrogen being 14, and that of chlorine 35.5. If now we bring together under these conditions of temperature and pressure two liters of hydrogen and one of oxygen gas, no change takes place until by the intervention of flame or the electric spark, or more slowly by the action of spongy platinum, their union is effected, with dissipation of radiant energy. The product of the integration of the two gases may exist at 0° either as solid ice or as liquid water. This latter at 100°, overcoming the atmospheric pressure of 760 mm., passes into water vapor, which at higher temperatures is subject to the common law governing the thermic expansion of gases, but at length reaches a point at which at standard pressure it undergoes heterogeneous disintegration, being resolved into its

[1] Miller. Chemical Physics, 3d edition.   [2] L. E. & D. Philos. Magazine (5), **13**, 548.

constituent gaseous elements.   The weight of a liter of water vapor
is the sum of the weights of a liter of hydrogen and half a liter of
oxygen, the volume of the latter, as well as the specific characters
of both, having in the act of integration been lost in that of a new
species, so that the weight of a liter of hydrogen at 0° and 760
mm. being unity $=$ 1.00, that of a liter of water vapor reduced by
calculation to the same standard temperature and pressure $=$ 8.98.
But as the combining weight for water vapor, or in other words its
integral weight, is found to be twice that number, or 17.96, its
volume is represented by two liters.   It is thus, in the language of
A. W. Hofmann, dilitral. When, in the older notation, the volume
of eight parts of oxygen was assumed as the unit, $O = 8$, water
vapor, then written H_2O_2, was said to consist of four volumes of
hydrogen and two of oxygen condensed into four volumes of vapor.

8. The condensation which appears in the union of hydrogen
and oxygen gases to form water vapor has been defined as inter-
penetration, but is more properly an identification of volume, or, to
use Herbert Spencer's term, an integration of the two combining
gases.   When, however, a liter of hydrogen is mingled within a
liter of chlorine gas at the standard temperature and pressure, the
two unite with violence by the action of sunlight, of flame, or the
electric spark, and form two liters of chlorhydric acid gas ; the first
action of light, according to recent observations of Pringsheim,
producing a sudden and transient increase of volume (due
perhaps to a disintegration of the chlorine, which marks a stage in
the chemical process).[1]   The properties of the combining gases
are lost in those of the new compound, but, contrary to the gen-
eral law of chemical union, in which integration is attended by con-
densation, there is no loss of volume.   We have in this case for
the weight of a liter of the newly formed gas, not the sum of the
weight of a liter of hydrogen and a liter of chlorine, but one
half of that sum, or 18.25 times that of the liter of hydrogen.

8. Further light is shown upon this process by the history of
the related fluorhydric acid gas, which at and near 100° has a
density corresponding to HF. At about 19°, however, it is
reduced to a liquid at the ordinary pressure, and between 20° and

[1] Pringsheim, L. E. D. Philos. Magazine, Dec. 1887, from Wiedemann's Annal. for Nov.
1887. The writer had already suggested that "the power of flame, or the electric spark, to
effect the sudden union of chlorine and of oxygen with hydrogen, may be due to the effect of
intense heat in separating momentarily into simpler forms portions of these gases, etc." (A
New Basis for Chemistry, §57.)

30° yields, according to Mallet, a gas or vapor corresponding to H_2F_2, which by a slight elevation of temperature is readily transformed into $2HF$. This gaseous compound of greater density is what in accordance with the general law of chemical integration should be formed by the union of H_2 with F_2, and we may conclude that in the case of chlorhydric acid a similar compound, H_2Cl_2, is possible, which, however, would at once pass, at the ordinary temperature and pressure, into $2HCl$.

9. The capacity of the compound of fluorine and hydrogen to exist at the ordinary pressure in two gaseous states of unlike density serves to illustrate many similar facts in the history of elemental and compound species alike. Among the latter are the well known examples of acetic aldehyde, acetylene, pentine, and the various polymers of these. Among the elements, oxygen when liberated in the decomposition of water by fluorine (Moissan), or by electrolysis, appears in part in the gaseous modification known as ozone, having a density one and a half times that of the ordinary form of oxygen—that is to say, its weight is not sixteen times but twenty-four times that of hydrogen at the same temperature and pressure. The effect of the electric spark, and of the silent electric discharge, to convert a considerable portion of dry oxygen into ozone, which is, however, rapidly resolved by heat, and more slowly at ordinary temperatures into common oxygen, $2O_3 = 3O_2$; the case of selenium, which yields a condensed vapor, Se_3, resolvable at a higher temperature into Se_2; and that of the triply condensed sulphur vapor, S_6, now found to be convertible at higher temperature into S_2, corresponding to the normal oxygen, O_2; the vapors of phosphorus and arsenic, represented by P_4 and As_4, partially changed by heat into P_2 and As_2; and finally, the vapors of bromine and iodine, Br_2 and I_2, which alike by heat and by the explosive and silent electric discharge are more or less completely changed into unstable vapors of Br_1 and I_1—are all illustrations, then unknown, of the same principle of greater or less gaseous condensation, first advanced from theoretical considerations by the present writer in 1848 (§§2, 3). The fact that the silent electric discharge at a low temperature effects a similar disintegration in the vapors of bromine and iodine to that wrought by great heat or by the electric spark, thus producing a change apparently the reverse of that produced by the same silent discharge in oxygen gas, leads to the suggestion that the generation of ozone thereby may be

due to the momentary disintegration of a portion of oxygen, O_2, into $2O$, which at low temperatures unites with an unchanged portion to form O_3.

The examples above given will suffice to show that the principle of chemical change by integration and disintegration appears not only in the relations of unlike species with each other, as of hydrogen with oxygen, with fluorine, with chlorine, or with sulphur and iodine vapors, but also with these same simple gaseous species among themselves. In other words, the more elemental gaseous forms of oxygen, of sulphur, of iodine, of fluorhydric acid, and of hydrocarbonaceous bodies, unite with themselves by homogeneous integration to form new gaseous species differing in specific gravity and in other physical characters, which have been designated allotropic or polymeric forms. Thus the same principle applies alike to the union of similar and dissimilar species, to homogeneous and heterogeneous integration, or, in the language long since adopted by the writer, to *chemical metamorphosis* as well as to *chemical metagenesis.*

10. We have seen that while the unit of weight is represented by the liter of hydrogen at $0°$ and 760 mm., the unit of combination for the derived species, such as water vapor and chlorhydric acid gas, is represented by twice this volume, the species being, in the language of Hofmann, dilitral. The corresponding dilitral volume of hydrogen gas itself then becomes $H_2 = 2$, a fact which is indicated by applying to it the term diad or diatomic. To this type of condensation also belongs nitrogen gas, together with oxygen, chlorine, and the vapors of bromine and iodine in their ordinary conditions, that of sulphur above $800°$ and of selenium above $1200°$, that of tellurium, and probably that of antimony. Oxygen in the form of ozone, and selenium at low temperature, are triad or triatomic, while the ordinary vapors of phosphorus and arsenic are tetrad, apparently becoming diad at higher temperatures, and that of sulphur below $550°$ is hexad. Iodine vapor, as we have seen, may be metamorphosed into a monad species, in which its weight is not 127 times that of hydrogen gas at the same temperature, but one half that number; while the vapors of mercury and cadmium are known only in a monad form. A similar metamorphosis by expansion or homogeneous disintegration is, from analogy, possible for hydrogen at elevated temperature and reduced pressure; that is to say, the production

of a monad form of hydrogen, H, corresponding to monad cadmium vapor, Cd, and monad iodine vapor, I, and having for a liter at 0° and 760 mm. a weight of 0.0448 gram. Nor can we assign any reason *a priori* why the process of homogeneous disintegration may not go on still further, unless indeed it be limited by a process of heterogeneous disintegration which may resolve the hydrogen into two or more unlike species, as supposed by Grünewald to be the case in the solar chromatosphere.

11. The weight of a liter of water vapor is made up of that of a liter of diad hydrogen, H_2, with that of half a liter of diad oxygen; while the weight of a liter of chlorhydric acid gas includes only that of half a liter each of diad hydrogen and diad chlorine, or of a liter of monad hydrogen integrated with a liter of monad chlorine. Reasoning from compounds like this, it has been assumed that the weight of monad hydrogen, 0.0448 gram to the liter at standard temperature and pressure, is the smallest admissible, and that the weight of the element in a liter of any compound vapor or gas must be a multiple of this by some whole number; that of oxygen, if present, being in like manner not less than 7.98 times this same weight. The question arises whether we have as yet any experimental evidence of such homogeneous disintegration as should give in the liter of any vapor or gas at 0° and 760 mm., quantities of hydrogen or of oxygen not in accordance with these weights. In the vapor of ordinary water, in which the ratio by volume of $H : O = 100 : 50$, it is evident that there is no deviation from these values; but if, admitting the existence of an oxygenised water as described by Schützenberger, in which that ratio is $100 : 51$ ($1.0 : 8.14$ by weight), we suppose this to be converted into a homogeneous vapor containing in a liter 0.0896 gram of hydrogen, it is evident that the oxygen, being not 0.0896×7.98 but 0.0896×8.14, will be equal to one and one-fiftieth portions. Further evidence of the distinctness of such oxygenised water, and of a similar oxygenised carbon dioxide described by Schützenberger, is however to be desired before the existence of such dissociation can be established.

12. We have now considered two kinds of chemical union: (1) heterogeneous integration, or the identification of volumes of unlike species, and (2) homogeneous integration, or the identification of volumes of like species, in which consists the so-called polymerisation and most cases of allotropism. Both of these

modes of union have a wide range, dependent on pressure; and the gaseous species formed by the first process become, like the elements themselves, the subjects of the second process. The process of integration by successive steps gives rise to homologous or progressive series, as in the paraffines, the olefines, the acetylenes, the benzenes, and other hydrocarbonaceous series, in recognised species of some of which the coefficient of the carbon is not less than 30. In the olefines, $n(CH_2)$, the first term being the same as the common difference, all the succeeding members of the homologous series are polymers thereof, constituting what we have called *isomeric homologues*. This name serves to distinguish them alike from those homologous series in which the first term is unlike the common difference, and which are *anisomeric homologues*, and from those isomeric compounds which are formed by successive homogeneous integrations, and between which, as between the allotropic forms of the elements, there is no apparent homology or similarity of function.

Familiar examples of such allotropic derivatives of species, themselves formed by heterogeneous integration, are seen in the successive condensations or homogeneous integrations of pentine, of acetylene, of cinnamene, and of the aldehydes, some of which take place spontaneously or with very slight provocation not only in gaseous but in liquid species. Besides the olefines among the hydrocarbons, we find in bodies like the carbon-spars, $n(CMO_3)$, examples of what must be regarded as isomeric homologues, and perhaps, though less apparently so, in the different allotropic forms of the titanium and silicon dioxides, wherein that similarity of function which marks homology is either non-apparent, from their chemical indifference, or else is absent. The latter is evidently the case in many cases of compounds the empirical formulas of which present good examples of progressive series, as in the metallic oxides, sulphides, and arsenides. An illustration of this is afforded in the observed compounds of manganese with oxygen, among which are MnO, Mn_3O_4, Mn_2O_3, Mn_5O_8, MnO_2, MnO_3, Mn_2O_7, and MnO_4, which, however, with but two exceptions, are known to us not in gaseous species, but only in highly condensed forms.

13. As the higher hydrocarbons of the various progressive series are built up by the integration of successive units of CH_2 with the first term of each series, so the monovalent alcohols and

the corresponding ammonias are generated in a similar manner from H_2O and NH_3. The capacity of such integration, or, in other words, the fixing power of such an integer as H_2, HCl, or NH_3, is very great, and theoretically knows no limit. By this consideration our conception of so-called atomicity or valency, which for an element has been defined as "its atom-fixing power measured by atoms of hydrogen" (J. P. Cooke), is greatly enlarged. Thus measured, chlorine is made monovalent, carbon tetravalent, and sulphur, like oxygen, divalent, although from its union with O_3 its hexavalence has been affirmed, a view which is sustained by the hexiodide of sulphur of Landolt, SI_6, and by the crystallised artificial sulphide of iron and nickel of Mackintosh (SFe_4Ni_2), while from the described iron sulphide, SFe_5, its octovalency would follow. Indeed, as there is reason to believe that the compounds of metallic iron formed in the blast-furnace with much smaller proportions of sulphur are homogeneous, it may be maintained that there is no limit to the valency of sulphur save that determined by the integral weight of the element on the one hand and that of the very highly condensed species known to us as molten iron on the other. Similar conclusions follow from the solution of carbon in the same metal, forming therewith compounds in which the hardness, fusibility, and magnetic relations of the metal are modified in a notable manner. The characteristic properties of the apparently homogeneous compounds of small proportions of both silicon and phosphorus, alike with iron, with copper and with other metals, and those of various metallic alloys, will at once suggest themselves to the chemist. In this connection may also be mentioned for illustration the solution of oxygen in molten copper, and that of the same gas in melted silver, forming a compound stable at high temperatures, but disintegrated on cooling at the ordinary pressure.

14. The power of fixing hydrogen possessed by various metals is not less instructive. The amount retained by palladium corresponds to Pd_2H, while potassium and sodium form therewith compounds of a certain stability, represented respectively by K_2H and Na_2H_2.[1] The capacity of the latter compounds to unite with smaller additional quantities of hydrogen, and that of other metals to combine with small amounts of the same element, show that the limit to be assigned to this power of fixing hydrogen by various metals presents as wide a range as that

[1] Troost and Hautefeuille, Comptes Rendus de l'Acad. des Sciences 28, 968.

observed by the metals for sulphur, phosphorus, silicon, or carbon. The fixation of bodies in chemical union or solution is not the prerogative of one element rather than another, as the popular statement of the doctrine of valency would seem to imply. The question of the stability of a chemical compound, whether formed by homogeneous or by heterogeneous integration, is one of temperature and pressure ; and heat, which readily effects the disintegration of the hydrides just mentioned, decomposes, either wholly or partially, at the atmospheric pressure, many metallic oxides. That the amount of one body retained in union with another is thus dependent on temperature, the pressure being constant, is well illustrated by the experiments of Spring on the arsenides of cadmium. The native metallic arsenides have for 100As quantivalent ratios for the metals represented by 33.3, 60, 66.6, 100, 150, 300 and 500, the latter $= 1:5$ being generally regarded as representing the maximum fixing power or atomicity of arsenic, hence designated as pentavalent. When, however, cadmium is fused with an excess of arsenic at a low red heat, a large part of this is volatilised, and there remains a very hard metallic body giving essentially the ratio $1:6$. It was not found possible to get by way of fusion a compound retaining a larger amount of arsenic, and this for the evident reason assigned by Spring, that "at the elevated temperature at which the combination of cadmium and arsenic takes place under ordinary pressure, the tension of dissociation is such that an arsenide is produced containing but little arsenic."[1] At ordinary temperatures, on the contrary, or under strong pressure, we have not to reckon with this tension of dissociation, and we readily get combinations containing a larger proportion of the volatile element. It is not the metal-fixing power of the arsenic, the oxygen, the sulphur, or the hydrogen, but rather the power of the metal to fix these more volatile elements under various conditions of temperature and pressure which we have to consider.

15. The ideal gas responds perfectly to external pressure, obeying implicitly Boyle's law ; the ideal solid is, on the other hand, theoretically incompressible. Gas and solid are, however, alike expansible by heat, and this dynamic change of volume by thermic expansion, which is regular and constant, is thereby distinguished

[1] Formation de quelques arséniures métalliques par l'action de la pression. 1883. Proc. Roy. Acad. Belgique (3), 5, No. 2.

from changes of volume from chemical metamorphosis, which are periodic. Thus, at the standard pressure, water below 0° is a solid, while from 0° to 100° it is a liquid, and above this point a vapor, which, so far as observed, has, like the liquid, its own nearly constant rate of thermic expansion. The vapor of sulphur, however, which from 450° to 550° has a density ninety-six times that of hydrogen, assumes above 800° a density only thirty-two times that of hydrogen. In the case of iodine-vapor, and of the vapors of fluorhydric acid, of nitric peroxide, of acetic acid, of acetic aldehyde, of many hydrocarbons, and of solids which like arsenic, phosphorus, and tin undergo allotropic transformations, we see examples of the same periodic chemical changes.

16. The question of greater or less density of gas or vapor for elements, and for so-called polymeric species, as compared with that of the hydrogen unit, is a question of greater or less homogeneous integration. Moreover, the gaseous, liquid, or solid condition is theoretically wholly dependent on temperature and pressure, as pointed out in §6. It is known that liquid species, if not subject to heterogeneous disintegration by heat, pass thereby, under increased pressure, into vaporous forms far denser than the normal vapors, which, while having the character of condensed or polymeric species, are stable only within certain narrow limits, and alike by increase of temperature and by diminution of pressure are changed, through homogeneous disintegration, into less condensed vaporous species. The genesis and the transformations of these heavy vapors thus imply a chemical process analogous to that observed in the denser and lighter vapors of sulphur, iodine, fluorhydric acid, nitric peroxide, acetic aldehyde, and acetic acid.

W. Allen Miller long since pointed out that the dense vapors of ether and alcohol formed just above the critical points of these liquid species have tensions far less than belong to the normal vapors, and, moreover, that the abnormally dense vapors of these liquids on augmentation of temperature not only present a much greater rate of expansion than air or water vapor, but, instead of being like these constant therein, show a rapidly increasing coefficient of dilatation.[1] These phenomena, as we have elsewhere remarked,[2] are in accord with those presented by sulphur, which, near its point of condensation, yields a dense hexad vapor readily

[1] Miller. Chemical Physics, 3d edition (1863).
[2] A New Basis for Chemistry, 2d edition, §117.

disintegrated at a higher temperature (and doubtless also by reduced pressure) into a less dense diad vapor. Applying, then, Boyle's law to the tension of ether vapor as observed just above its critical point, we find it to be not the normal vapor, but a highly condensed polymer which, by increase of temperature, is metamorphosed into less and less condensed species, as shown by the very rapid increase of the elastic force as compared with that of air under similar conditions of temperature and pressure.

In illustration of this point we may note that Ramsay and Young have lately observed that the vapor of alcohol at 243° has a tension of only 63 atmospheres and a specific gravity of not less than .280, water being 1.000. This corresponds to a fourfold condensation, $4(C_2H_6O)$, since the normal vapor of alcohol calculated for that temperature and pressure should, according to Boyle's law, have a specific gravity of .0684, or but one fourth of the number observed.

17. The progressive stages which in sulphur, iodine, fluorhydric acid and acetic acid are marked in the process of homogeneous disintegration by heat at the ordinary pressure, do not, however, occur in the cases of ether, alcohol, water, and similar volatile liquids, except when these are heated under increased pressure ; conditions under which all liquids not thereby exposed to heterogeneous disintegration may theoretically assume the gaseous state. The intermediate forms in the metamorphosis of volatile species are of very different degrees of stability, and while in many cases capable of existing at the ordinary pressure through a certain range of temperature, in others exist only within such narrow limits of temperature and pressure that we are led to conjecture from analogy that within still narrower limits there may exist many other intermediate species hitherto unknown and unsuspected. It may even be supposed that every variation in pressure acting upon compressible species gives rise to some passing chemical change too fugitive to be detected. It is known that variations in pressure control the production of allotropic forms in the case of solids, and may we not from analogy expect the same principle to apply in the action of pressure upon all bodies which depart from the theoretical elasticity of the perfect gas ? The ideal gas responds perfectly to every variation of pressure, according to Boyle's law, while the ideal solid is on the contrary incompressible (§15), but the representatives of both of these can exist only within certain limits of temperature and pressure.

18. The seeming continuity of the liquid and the gaseous states of matter, as seen in the dense vapors discovered by Cagniard de Latour, and the fact that gaseous matter by successive condensations under great pressure assumes at high temperatures a condition not of liquidity, but of dense gas or vapor, as set forth by Andrews, receives a remarkable illustration in the discoveries of Hannay and Hogarth.[1] These chemists have found not only that solutions of salts in alcohol and ether have their critical points, above which they pass integrally into the state of dense vapors, but that the dense vapors of the solvent liquids themselves have, like condensed hydrogen gas, the power to take into solution various solids. The fact that water (and probably watery solutions also) will pass into the state of dense vapor not far from 400° (as long since shown by Cagniard de Latour), and that this vapor is, moreover, as found by the authors just cited, a solvent alike for silica, alumina, and zinc oxide, is one which throws great light on many problems in geogony and physiological mineralogy. It leads us to conclude that liquid water does not exist in highly heated rocks at considerable depths from the earth's surface, where, however, it may be present either in chemical combination, reducing their fusing point, as shown in the late researches of Tilden and Shenstone, or liberated, and pervading them as a dense vapor, holding dissolved mineral elements to be subsequently deposited as crystalline species. The above facts serve to show that a solution is really an integral chemical compound, in accordance with the view long maintained by the author.[2]

19. The law of volumes prevails in all known cases both of homogeneous and heterogeneous integration among gases and vapors, in the changes of oxygen, and of the vapors of iodine and sulphur, as in those of fluorhydric acid, of aldehyde, and of pentine and its polymers, as well as in the not less remarkable condensations or polymerisations of acetylene. All analogy leads us to extend this law to the still greater condensations observed in the denser vapors into which liquid species, above their critical points, are resolvable, and to the further condensation of the vapors into liquid and solid forms—to assume, in fact, that the law of combination by volume, like that of combination of weight (with which, so far as experiment goes, it is indissolubly linked), is universal.

[1] Hannay and Hogarth, Proc. Royal Soc. London **29**, 324, and Chemical News **12**, 103-106; also, A New Basis for Chemistry, 2d edition, §§120, 121.

[2] A New Basis for Chemistry, §12.

The coefficient of condensation in the case of gases and vapors is readily found by comparing the densities of the respective species at standard temperature and pressure, in the way well known to chemists ; the weight of a given volume of hydrogen gas at that temperature and pressure being the unit. For the liquid and solid species formed by the homogeneous integration of these gases and vapors, as we have elsewhere endeavored to show, the weight of the same volume of the newly formed species at the temperature of its production under the standard pressure is to be taken as the term of comparison, either with that of the vapor or gas calculated for 0° and 760 mm., or finally, with the weight of an equal volume of hydrogen gas at the same temperature and pressure.

As declared by the writer in 1853, "the doctrine of chemical equivalents is that of the equivalency of volumes "; in other words, the law of volumes, like the law of weights, is universal, and for all species—liquid, solid, or gaseous—the volume, under proper conditions of temperature and pressure, is the same. The volume being then a constant quantity, the integral (or so-called equivalent or molecular) weight of any species, whether gaseous, liquid, or solid, is its specific gravity, hydrogen gas being unity.

20. The advantages to be gained by establishing a single unit for specific gravity, and by substituting alike for water at its maximum density (in the case of liquids and solids) and for air at 0° and 760 mm. (in the case of gases and vapors), hydrogen gas at the same temperature and pressure (a plan first indicated in the writer's volume entitled " A New Basis for Chemistry "), were urged in a paper entitled " Chemical Integration," read before the National Academy of Sciences in April, 1887, and published in the *American Journal of Science* for the following August. They were further insisted upon in a paper on " Integral Weights in Chemistry," read before the British Association for the Advancement of Science at Manchester, in September, 1887, and published in the *London, Edinburgh and Dublin Philosophical Magazine* for October of the same year. The integral weights of all gases and vapors are evidently their specific gravities, hydrogen being unity ; and since water itself is the unit of specific gravity, adopted for convenience, for all liquids and solids, it becomes of the first importance to determine its integral weight. The weight of a liter of hydrogen gas (H_2) at 0° and 760 mm. being approximately 0.0896 gram, and

that of a liter of water at 100° (its temperature of formation at 760 mm.) 958.78 grams, we have :

$$0.0896 : 958.78 :: 2 : x = 21400.3.$$

Taking Regnault's figure for hydrogen = 0.089578 gram, the weight of a liter of water vapor ($H_2O = 17.96$) calculated for the same temperature and pressure = 0.8044 gram ; we have then :

$$0.089578 : 958.78 :: 2 : x = 21406.6$$
$$0.8044 \quad : 958.78 :: 1 : x = 1191.9.$$

Of these, the last equation gives the coefficient of condensation for water, and if, rejecting the fraction, we assume water to be 1192(H_2O), we have $1192 \times 17.96 = 21408$. In the uncertainty which still prevails as to the exact weight of oxygen, hydrogen being unity,[1] we may safely assume in the calculation of their integral weights from the observed densities of other liquid and solid species, the first-found number, or 21400, as a sufficiently close approximation to the integral weight of water.

21. As regards the further history of the views just stated, it was pointed out in the first edition of the author's " New Basis for Chemistry " (§§66, 67) that in applying to water the well known formula for calculating the so-called atomic volume, $p \div d = v$, while d is its density at 4°, which is the unit of specific gravity for liquids and solids, p is the equivalent weight of its vapor, which is also its density, hydrogen being the unit. Hence the relation of $d : p$ involves the relation of the density of water to that of its vapor, and finally to that of hydrogen gas ; and thus enables us to determine the amount of contraction of H_2O in passing from the gaseous to the liquid state, or, in other words, its coefficient of condensation, v being the reciprocal of this coefficient. It was then said, "the question to be settled in fixing the equivalent weight of water is to know its specific gravity as compared with hydrogen gas, or with steam."

In applying this method, the density of steam at 100° as compared with water at 100° having, for the reasons given, occupied the writer's attention, he, by inadvertence, took the densities at this temperature, and was thus led to assign to water the erroneous formula, 1628(H_2O), which, assuming $H_2O = 17.9633$, gave an integral

[1] *Vide* The Relative Values of the Atomic Weights of Hydrogen and Oxygen. Cooke and Richards, this Journal **10**, 81, and Proc. Amer. Acad. 1887, **23** ; also Rayleigh, Proc. Roy. Soc. London, 1888, **43**, 356.

weight of 29244. In resuming, however, in §95 of the same volume, the question of the density of liquids and solids taken with water at 4° as unity, it was declared to be " necessary to refer them to a common standard of density, or, in other words, to determine the relation of density between water and hydrogen gas "; d being " the density of water at 4°, and p that of hydrogen at 0°." Soon after, in the paper on " Chemical Integration " referred to in §20, it was said that " instead of the weight of atmospheric air at 0° and 760 mm. . . . as the standard unit of specific gravity for all gases and vapors, hydrogen at the same temperature, which gives us the unit of integral weight, would seem to be the natural unit of specific gravity for all bodies whatsoever"; and again, in comparing the densities of liquid and solid species " with the density of the hydrogen unit, H_2, we get the specific gravity of these bodies, the diad integer of hydrogen at 0° and 760 mm. being unity." Still further, in the second paper cited in §20, it was said, " hydrogen, as the lightest known species, is the unit of integral weight in chemistry, and a liter of this gas at 0° and 760 mm. being assumed as a unit of volume for all species, the weight of a liter of any other vapor or gas at the standard temperature and pressure is its integral weight "; while the weight of the same volume for liquids should be taken " at the temperatures at which they are generated by the metamorphosis, through condensation, of the corresponding gaseous species." " In like manner, the weight of solids should, theoretically, be determined at the temperatures at which they are generated by the metamorphosis of gaseous or liquid species "; in other words, we should take for any solid species, " the weight of the same volume at the highest temperature at which that species can sustain without undergoing a change of state." Notwithstanding all these repeated statements, the erroneous value for the integral weight of water, calculated by comparing hydrogen gas, water vapor, and water itself, at the common temperature of 100°, was, by an oversight, retained until corrected by the writer in a note on "The Integral Weight of Water " in the *London, Edinburgh and Dublin Philosophical Magazine* for April, and in the *American Journal of Science* for May, 1888.

22. In the paper on " Integral Weights in Chemistry " was, moreover, considered at some length the relation of the regular thermic changes in volume alike of water and of most solid species to the question of integral weights and specific gravities. It follows from

what has been said above that, theoretically, the weight of the volume of water should be taken at 100°, and that of most solids, such as metals, ores, gems, and spars, at temperatures much more elevated. But we have sought to show by comparison of the cubic expansion of water between 4° and 100°, with the much smaller rates of expansion of the solid species in question between 4° and the temperatures of their chemical change by heat, that the resulting errors in the determination of specific gravities at ordinary temperatures to a considerable extent balance each other, and further, that the imperfections and impurities of most natural and artificial species introduce in such determinations " possible deviations in the one and the other direction as great as those due to the different rates of expansion of water and these species, so that we may take the approximate specific gravities got with water at 4° (or better, at 15.5°) as an available basis for fixing the integral weights of most solid species."

23. To illustrate alike the mode of calculating the integral weights of solid species, and the use and inter-relations of the two standards of specific gravity mentioned above, namely, water at ordinary temperatures and hydrogen gas at 0° and 760 mm., we may take the case of a crystalline species formed by the condensation of an unknown number of volumes of a theoretical calcium carbonate, $CCaO_3 = 100$. The integral weight of water being in round numbers (§20) 21400, and the specific gravity of the calcareous species (water 1.000) 2.730, we have $21400 \times 2.730 = 58422$. Dividing the integral weight thus found by that of $CCaO_3 = 100$, we find the number of volumes of this hypothetical carbonate condensed in one volume of the calcareous species, or, in other words, its coefficient of condensation, to be 584.22. Rejecting the fraction, we have for this species, which is calcite, $584(CCaO_3) = 58400$, with a theoretical specific gravity of 2.729.[1] The relation between the integral weight of the calcium carbonate $CCaO_3 = 100$ (hydrogen, 1.0, being unity) and the specific gravity of the calcite (water $= 21400$, being unity), is got by the equation

$$2.729 : 100 :: 1 : x = \frac{p}{d} = v = 36.643.$$

This, the so-called molecular or atomic volume of $CCaO_3$ as it

[1] The equivalent weight of $CCaO_3$ is here calculated with $O = 16$, substituting for which the value $O = 15.96$, we have instead of 100 the number 99.88. This gives for $584CCaO_3$, instead of 58400, an integral weight of 58330, corresponding to a specific gravity of 2.7357 instead of 2.7290, a difference so small that it may be neglected as within the limits of error.

exists in calcite of such density, is the reciprocal of the above
coefficient of condensation, since $36.643 \times 584 = 21399.5$.   But
calcite of this density is 58400 times heavier than the same volume
of hydrogen at $0°$ and 760 mm., so that substituting this value (its
specific gravity on the hydrogen basis) for the first term in the
above equation, we find the value of v (H $= 1.0$) to be $= 0.0017123$,
and we have :

$$1 : 21400 :: 0.0017123 : 36.643.$$

In like manner, water, $1192(H_2O)$, taking itself as the unit of
specific gravity, gives $v = 17.96$, while on the hydrogen basis, with
an integral weight of 21400, we find $v = 0.000839$ nearly.   But
$1192 \times 0.000839 = 1.00088$.

23. In considering, in 1863, the question of differences in con-
densation as exemplified between the various carbon-spars, horn-
blende and pyroxene, fibrolite and cyanite, and especially between
meionite and zoisite, it was said, "the augmentation in density, in
hardness, and in chemical difference which is seen in this last
species [as compared with meionite] is doubtless to be ascribed to
a more elevated equivalent, or, in other words, to a more condensed
molecule."[1]   Again, in 1867, in discussing these and other
examples in mineral species, it was said, "the hardness of these
isomeric or allotropic species, and their indifference to chemical
reagents, increase with their condensation, or, in other words,
vary inversely with their empirical equivalent volumes ; so that
we here find a direct relation between chemical and physical prop-
erties."[2]   The conclusion then reached was, in fact, that for related
solids, hardness and chemical indifference increase with the con-
densation of the species, or, in other words, vary *inversely* as their
empirical equivalent or so-called atomic volumes, represented by v :

$$\frac{atomic\ weight}{specific\ gravity} = atomic\ volume = \frac{p}{d} = v.$$

This is in accordance with earlier observations as to the tenacity
and hardness of metals and alloys.   Wertheim, from his experi-
ments, concluded (as Guyton Morveau had long before) that the
order of the common metals for tenacity and for hardness is prac-
tically the same, and announced in 1841 that the tenacity varies

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[1] Comptes Rendus de l'Acad. des Sciences, June 29, 1863, and in English, Amer. Jour.
Science 36, 426.
[2] Amer. Journal Science 43, 203.   See further, A New Basis for Chemistry, chapter VII,
and also Appendix to the 2d edition.

directly as the quotient of the specific gravity divided by the atomic weight:

$$\frac{specific\ gravity}{atomic\ weight} = \frac{d}{p} = \frac{1}{v}\ .$$

This conclusion was confirmed by the studies of Calvert and Johnson, in 1859, on the hardness of metals and alloys ; by those of Karmarsh on the tenacity of metallic wires ; and by those of Bottone, in 1873, also on the hardness of metals ; the latter maintaining that for homogeneous bodies of uniform texture, hardness and tenacity vary together in accordance with the law enunciated by Wertheim.[1] The law thus arrived at by various investigators for the hardness and tenacity of metals and alloys is identical with that independently deduced by the author, not only for the hardness but for the indifference to chemical changes, of related silicates, carbonates, and oxides.

24. We have sought in the preceding pages to set forth and to explain what may be regarded as the fundamental facts of chemistry, by an extension of the well known and verified laws of combination by weight and volume. In doing this, it has not seemed necessary or in any way advantageous to invoke the aid of the atomic hypothesis. This, which was adopted in 1808 by Dalton to explain the facts of definite and multiple proportions observed in chemical changes, has since been greatly extended and modified in the effort to apply it to many phenomena then unknown. Molecules being assumed to be built up of atoms, it is supposed, in the language of Lothar Meyer, one of the most able and learned exponents of the hypothesis, that while " each monovalent atom possesses only a single position in space by which another atom can be held by it in stable equilibrium," the polyvalent atoms may have " four, five, or six such positions," or points in space. The atoms themselves " are in a state of active motion, with these points as centres of equilibrium. The motion may be rotary or oscillatory. In those cases in which an atom fills two or more of these points it is considered to oscillate between, or, rotating, to pass through these centres." These atoms are furnished with " bonds," " links," or " hooks," and are joined together by various modes of

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[1] See, in this connection, The Hardness of Metals, by Thomas Turner, Chemical News, April and May, 1887. It may here be remarked that compounds of metals with sulphur, phosphorus, carbon, and silicon often differ greatly, alike in dynamical and in chemical characters, from the metals themselves, as may be seen in the increased hardness and tenacity of certain compounds containing even small portions of some of these elements (§13).

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"atomic linking" both single and double, forming "rings," "chain-like groups," "open chains," "closed chains," "branched chains," etc. Thus for example, "a branched series of atoms is obtained, composed of several linear chains. In the same way these branches can also divide, and the new branches may be united together by connecting links, forming ring-like or net-like structures." The author, however, tells us in a foot-note that the expression "ring-shaped" "need not be accepted as applying to space; it only indicates that the attractions between the atoms which maintain the coherence of the molecule form a continuous series."[1] In like manner Prescott states that "in the use of the chemical term, position," he will be understood to refer "not to arrangement in space, but to the order of the union of the atoms with each other."[2] Another distinguished American chemist has, however, lately assured us that the question of "atom-grouping has a mechanical as well as a chemical side," and notwithstanding the provisos above quoted, it seems impossible to divest the language which we have quoted from Lothar Meyer of a geometrical sense. Without speaking of the fancies of earlier writers as to the architecture of molecules, it is well known that Le Bel and Van't Hoff have speculated upon the supposed arrangement of the atoms of molecules in space, and that Wislicenus has lately made a further contribution in the same direction towards a hypothesis of the geometry of molecules.[3]

25. By such assumptions as the foregoing the modern atomistic chemistry seeks to explain the physical and chemical characters of species, which it regards as dependent upon forces and properties supposed to dwell in the individual atoms from which these are conceived to be built up. Structural formulas in accordance with this hypothesis may serve to explain the facts of definite and multiple proportions, of polymerism in vapors, and of the peculiar differences presented by such isomeric bodies as the primary, secondary and tertiary alcohols, $C_nH_{2n+2}O$. Assumed differences in "the order of the union of atoms with each other" may be made to account for the unlike genetic relations presented in their chemical changes by certain of these isomeric species, but there are other phenomena which it will require still further and purely

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[1] All the expressions here quoted are from the chapter on the Law of Atomic Linking, in the late excellent translation by Bedson and Williams of the 5th edition of Lothar Meyer's Die Modernen Theorien der Chemie ; Longmans, 1888.

[2] Prescott, "The Chemistry of Nitrogen," J. Am. Chem. Soc., Sept. 1887, 133.

[3] See this Journal 9, 453.

gratuitous assumptions to explain by the atomic hypothesis. Such for example are the subtle differences which divide the amylic alcohol got by fermentation into two species, one optically active and the other inactive. These, though convertible the one into the other, present also minor chemical distinctions, and, moreover, transmit their optical characters to the derived valeric acids.[1] Similar chemical and optical unlikenesses appear in the limonenes, pinenes and camphenes, which are all apparently isomers of dipentine; and other examples of optical, crystalline and chemical differences meet us frequently in the study of isomeric and homologous bodies, which can hardly be explained by any constitutional or so-called structural formulas.

To indicate the essential differences which distinguish two substances having, it may be, the same centesimal composition and the same density, alike in the vaporous and the liquid or solid state, as in the instances above noted, they have been said by different writers to be unlike in " structure," or in " organization." The term structure, however, implies that the substance in question is put together or is built up by a certain arrangement of parts, while the term organization superadds the conception of such a subordination of parts to function as belongs to crystalline or to biotic structures. For these reasons it is conceived that the term " constitution," which implies no mechanical hypothesis, but simply refers to the character or the *essential form* of the species in question, is to be preferred. Chemical species are subject to constitutional changes, or, in the language of Andrews, to " internal disturbances," which alter to greater or less degrees alike their dynamical and their chemical relations. Such constitutional changes may manifest themselves in veritable metamorphosis by homogeneous integration or disintegration, and consequent change in integral weight; or in other cases by such slighter differences as have been signalised in the amylic alcohols and the various dipentines ; or as are seen in certain cases of crystalline dimorphism, which are apparently independent of any change in density. Were it possible to establish on valid grounds the existence of chemical molecules, built up by the putting together of the atoms in the fantastic arrangements supposed by the present highly complicated atomic hypothesis, further assumptions would still be required to account for these minor constitutional differ-

[1] See on this subject the studies of Pasteur, Pedler, and Chapman and Smith ; Watts's Dict. of Chemistry, 1st Supplement, *sub voce* Amyl Alcohols.

ences. Something radically different from this or any other mechanical hypothesis must, in the writer's opinion, be devised before we can hope to explain adequately the dynamical and chemical history of matter. Signs are not wanting that this famous hypothesis, so generally accepted by chemists since Dalton's time, is felt by many to be no longer adequate, and that, in the language of J. P. Cooke, it may be regarded as " only a temporary expedient for representing the facts of chemistry to the mind."[1] The fate which befell the corpuscular hypothesis of light, and now seems to menace the undulatory hypothesis, appears to await the atomic hypothesis in chemistry.

VIII.—THE SAFETY OF COMMERCIAL KEROSENE OILS.

By Spencer B. Newbury and W. P. Cutter.

A series of experiments were made by the writers a year ago for the purpose of determining the maximum temperature reached by the oil in the reservoirs of the most powerful modern oil lamps. A brief outline of the results of these experiments was published in the *Scientific American Supplement*, July 16, 1887. The writers found that the oil in modern lamps often reaches a temperature of 110° to 112° F., and strongly urged the use in these lamps of oil having a high flashing point, in order to avoid danger of explosion.

The legal regulations in regard to the flashing point of illuminating oils vary greatly in different parts of the country, certain States having no statutes on the subject, others requiring that no oils shall be sold which do not reach a certain standard of safety. In New York State no oil is allowed to be sold which flashes below 100° F. when tested in the manner prescribed by law, in the instrument known as the New York State Tester. Most of the prevailing legislation upon the subject is probably based upon the observations of Dr. C. F. Chandler, who sixteen years ago made a careful study of the question of the safety of burning oils.[2] Dr. Chandler found that the oil in the lamps generally in use at

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[1] American Journal of Science (1883) **26**, 310–316.   [2] Am. Chemist, Aug. 1872, 43.

that time, while burning in rooms at ordinary temperature, rarely reached 100° F., but nevertheless recommended the adoption of a legal standard of flashing point not lower than 120° F. In this connection he says,[1] "The point of 100° F. does not seem high enough to secure immunity from danger, though it may be said that very few, if any, accidents occur with oil which does not flash below this temperature."

If the standard of 100° was too low to afford protection with the old-fashioned single-wick burners, it must be far more inadequate at the present day when lamps are everywhere in use which raise the oil in the reservoirs to a point fully twenty degrees higher than that reached in the lamps which Dr. Chandler tested. In modern oil lamps with double wick or circular burner, the oil while the lamp is in use is often, probably generally, heated above its flashing point. It is evident, then, that the danger of explosion is constantly present while using these lamps with ordinary oils, unless, indeed, some other cause than temperature may contribute to the safety of oils which flash above 100°. It is not proved, for example, that the vapor of such oils can, at any temperature, form violently explosive mixtures with air. So far as previous experiments have shown, kerosene explosions may be due to the presence in oils of low flashing point, of small quantities of very volatile or gaseous hydrocarbons; these constituents may be absent in oils of high flashing test, these latter may therefore not be capable of exploding. In short, no clear statement has yet been made of the relation of the flashing point of oils to their capability of giving violent explosions with air. It was in the hope of establishing such a relation, and thus determining the value of the flashing point indications as a guarantee of safety, that the experiments described in this paper were undertaken.

The questions which presented themselves for study may be briefly stated as follows:

1. Will all the hydrocarbons of which burning oils are composed, when diffused in air in proper proportions, yield distinctly explosive mixtures? If so, at what temperature for each?

2. What are the most volatile constituents of ordinary kerosene, and how do the proportions of each of these lighter hydrocarbons affect the flashing point of the oil?

It is well known that it is difficult to produce explosive mixtures

[1] Johnson's Encyc., "Petroleum," 227.

of gases at will; the experiment of exploding marsh gas with air requires very careful adjustment of proportions, or no explosion results.

A series of hydrocarbons of nearly constant boiling point was obtained by careful purification and repeated fractional distillation of lighter petroleum products. The distillation was accomplished with the aid of a long Hempel tube. In testing the possibility of producing explosions with air with the several fractions, a strong glass cylinder 30 cm. high and with a capacity of 300 cc. was employed. This was immersed nearly to its mouth in a water-bath, by means of which the experiments could be made at any desired temperature. The amount of each hydrocarbon which could be completely burned by this volume of air was calculated, and the corresponding quantity of each fraction weighed out in a thin glass bulb about $\frac{1}{2}$ cm. in diameter. When a test was to be made, a little mercury was placed in the cylinder, the little bulb of hydrocarbon introduced, and the cylinder closed by a well-fitting stopper. By shaking, the bulb was then broken and its contents diffused throughout the air in the cylinder. The explosiveness of the mixture was tested by cautiously removing the stopper and applying a small flame to the mouth of the jar. The experiments were made with varying qualities of each hydrocarbon, and at different temperatures. It was found that the most violent explosions were obtained by the use of nearly the amount of the hydrocarbon which could be completely burned to water and carbon dioxide by the volume of air in the cylinder. It was shown at once, moreover, to the surprise of the experimenters, that sharp explosions could be obtained at ordinary temperatures with hydrocarbons of comparatively high boiling point, as for example with heptane, which boils at about the same point as water. The following table gives a summary of the results obtained:

Hydrocarbon.	Formula	B. P.	Source.	B. P. of Fraction.	Temperature at which explodes with air.
Butane . . .	C_4H_{10}	1° C.	C_2H_5I and Sodium.	1° C.	Ordinary.
Pentane (Iso) .	C_5H_{12}	30°	Petroleum Ether.	30°	"
Hexane . . .	C_6H_{14}	68°	" "	67–68°	"
Heptane . . .	C_7H_{16}	98.5°	"Abietene " (*Pinus Sabiniana.*)	98.5°	"
Octane . . .	C_8H_{18}	124°	Illuminating Oil.	125–130°	"
Nonane . . .	C_9H_{20}	149.5°	" "	148–150°	Between 150° and 212° F.
Decane . . .	$C_{10}H_{22}$	161°(?)		160–165°	Between 150° and 212° F.

Nonane and decane could not be made to explode with air at temperatures under 150° F., but by heating the bath to 212° F. distinct explosions were obtained. As these hydrocarbons seemed to mark the limit of the constituents of a safe oil, experiments were made under conditions similar to those which prevail in a burning lamp. A cylindrical copper vessel of about 300 cc. capacity was employed, provided with a loosely fitting cover through which a hole about $\frac{3}{16}$ inch in diameter had been bored. This was charged with a few drops of the material to be tested, and gradually heated in a water-bath, a small flame being applied to the orifice from time to time, as in the ordinary method of testing oils. The point of explosion was shown by a distinct puff which threw off the cover of the vessel. The results were more definite than those obtained by the use of the glass cylinder, and show that the legal limit as to flashing point lies between these two hydrocarbons.

Nonane exploded sharply at 79° F.
Decane " " " 104° F.

A sample of illuminating oil which showed a flashing point of 111° F. by the New York State tester gave, when tested as above, a distinct explosion at that temperature, 111° F.

The above experiments lead to the following conclusions :

1. All the paraffines up to decane, and probably also higher members of the series, may at suitable temperatures form explosive mixtures with air.

2. Oils which flash at a point considerably above the legal requirement may, under proper circumstances, give violent explosions at their flashing temperature.

3. An oil consisting of pure decane, $C_{10}H_{22}$, would be accounted a safe oil by the legal flashing point test of New York State, while one consisting of nonane would be below the standard.

In order to determine what are the lowest hydrocarbons present in ordinary burning oil, a sample of commercial " water-white " oil of excellent quality, showing a flashing point of 108° F., was carefully distilled, at first in a vacuum, and the lighter portions repeatedly fractionated by means of a Hempel tube. Two kilograms of oil yielded 30 grams of a distillate boiling at 110°–130° C., which on further rectification proved to be chiefly octane ; and 100 grams, boiling at 130°–160° C., which appeared to consist principally of nonane and decane. Only traces of hydrocarbons

of lower boiling point than octane were present. The addition of
5 per cent. of heptane to a sample of this oil lowered the flashing
point to 97°. A specimen of "mineral sperm" oil which flashed
above 212° F. was treated with different proportions by weight
of pentane, hexane, and heptane, and the reduction of the flashing
point noted.

Mixtures of Mineral Sperm Oil with Light Hydrocarbons.

Mineral sperm oil 95 per cent., pentane 5 per cent., flashes 110° F.

"	"	" 90	"	"	"	10	"	"	"	ord. temp.
"	"	" 95	"	"	hexane	5	"	"	"	110° F.
"	"	" 90	"	"	"	10	"	"	"	ord. temp.
"	"	" 95	"	"	heptane	5	"	"	"	145° F.
"	"	" 90	"	"	"	10	"	"	"	110° F.
"	"	" 83	"	"	"	15	"	"	"	96° F.
"	"	" 80	"	"	"	20	"	"	"	ord. temp.

It is evident, therefore, that the low flashing point and danger
of oils may be due not to the presence of small quantities of very
volatile products, but rather to the large proportion which they
contain of constituents of moderately high boiling point.

The burning test which determines the temperature at which a
sample of oil may be set on fire and will burn in an open vessel,
has been generally conceded to be unreliable as an indication of
safety. Nevertheless, the laws of New York State prohibit
the sale of oil which burns below 300° F. An oil may show
a very high burning test and yet be of low flashing point and
therefore extremely unsafe. This is especially the case with oils
which consist of a mixture of very heavy and very light hydro-
carbons. The more nearly homogeneous an oil is in composition
the closer the flashing and burning points will approach each
other. For example, the fractions corresponding to nonane and
decane used in the experiments described above take fire at a tem-
perature but little above their flashing points.

Nonane flashes 79° F., burns 110° F.
Decane   "   104° "   "   136° "

The flashing point of an oil is also, as is well known, dependent
not only on the proportion of light constituents present, but upon
the character of the oil as a whole. An unsafe oil may be brought
up to legal standard by adding to it a sufficient quantity of heavy
lubricating oil, but such a heterogeneous mixture will be of poor
quality for burning purposes. It is doubtless this which has led
manufacturers to make the oft-repeated claim that a high flashing

point is inconsistent with good burning qualities. If refiners would be content to make a little less oil, leaving out some of the benzine and some of the lubricating oil as well, there would be no difficulty in producing illuminating oils of high flashing point and excellent illuminating power. The well known Astral oil, which flashes at 125° F., is a standing protest against the claim of superior burning qualities for low-grade oils. This is simply the *heart* of the burning oil freed from both lighter and heavier deleterious ingredients. Tests made by the authors have shown that the above mentioned brand burns admirably in modern lamps, and by photometric tests gives results fully equal to any other oil in the market.

We are at present engaged in a series of experiments to determine the relative value as illuminating agents of the different hydrocarbons composing kerosene. The results of these experiments will form the material of another communication.

Only a very small amount of volatile material requires to be removed from an oil of ordinary character in order to raise its flashing point materially, as the following experiment shows.

One kilogram of an oil flashing at 108° F. was placed in a flask, and a gentle current of air at ordinary temperature aspirated through it during 24 hours. At the end of that time the oil was found to have lost 28 grams, or 2.8 per cent. in weight, and showed a flashing point of 116° F. Treatment of ordinary oils by a somewhat similar process would doubtless be effective in making them materially safer, and would probably add but a fraction of a cent per gallon to their cost.

It would be too much to expect of refiners that they should furnish oils of much higher flash test than they are required to do by law. The passage of a statute raising the legal standard to 120° would, however, cause no serious hardship to manufacturers, and would effect a saving of life and property which would far outweigh the very slightly increased cost of burning oil. It has been urged that with such a law manufacturers would simply add heavier products to their oils and thus bring them up to the legal standard, to the detriment of their burning qualities. This would, however, be in opposition to their own interest, since oils of high flash and excellent quality are already in the market and are extensively used.

The experiments described above show conclusively that an oil heated above its flashing point is dangerous, whether that point be

high or low.   There can, therefore, be no doubt that in using kero-
sene of ordinary quality in the powerfully heating lamps which are
now common, we are dependent for our safety upon the accurate
construction of the burners, which render it difficult for the explo-
sive vapors in the lamp to become ignited.   An oil which flashes
below 120° F. is not safe to use in these lamps, and with oils of
ordinary grade the conditions of explosion are constantly present.

IX.—APPARATUS FOR FRACTIONAL DISTILLATION IN VACUUM.

By Spencer B. Newbury.

The subject of distillation under reduced pressure has been
thoroughly discussed by Anschütz,[1] and the apparatus recom-
mended in that author's pamphlet certainly appears to leave little
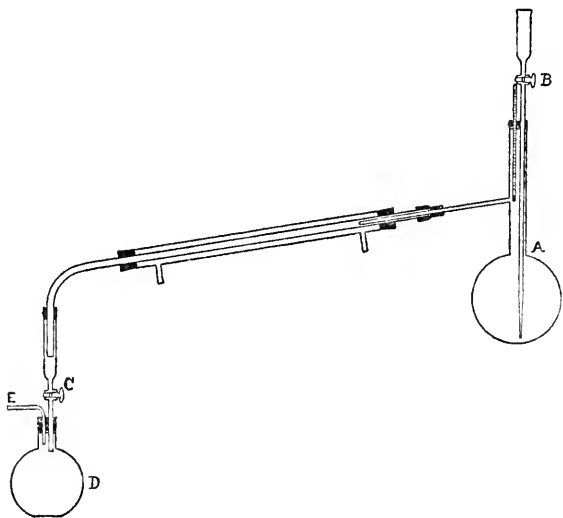
to be desired in respect of convenience or efficiency.   The arrange-
ment shown in the accompanying figure has, however, the advan-
tage that none of its parts require to be specially constructed, and
the whole may easily be put together from apparatus to be found
in almost any laboratory.

[1] Ueber die Destillation unter vermindertem Druck, Bonn, 1887.

A distilling bulb, *A*, is provided with a double-bored rubber stopper, through one aperture of which passes a thermometer, and through the other the tube of an ordinary separating funnel, drawn out at its lower end to a capillary tube which reaches nearly to the bottom of the flask. The outlet tube of the bulb is connected with a condenser, as shown in the sketch. The inner tube of the condenser is bent down at its lower end and terminates in a second separating funnel, the tube of which passes into the receiver *D*; from the latter a small bent tube *E* serves to connect the apparatus with an ordinary Bunsen filter-pump provided with a manometer.

The substance to be distilled is placed in *A*, the air exhausted to constant pressure, and the distillation commenced by heating *A* in a bath of water or paraffine. A gentle current of air is allowed to bubble through the liquid by slightly opening the stop-cock *B*; this may be so slight as to have no effect on the pressure, and serves to prevent the " bumping " of the liquid. As soon as one fraction has been collected in the receiver the stop-cock *C* is closed, air is admitted through *E*, and the flask *D* removed and replaced by another. This is then emptied of air, the stop-cock *C* opened, and a second fraction collected. In this manner a series of fractions may be obtained without the necessity of admitting air to the whole apparatus when the receiver is changed. (This is essentially the arrangement described by Thörner.[1])

The separating funnel *B* serves not only as an inlet tube for air, but also for the introduction of the successive fractions for redistillation without loss of vacuum. By the use of this simple device complete fractional distillation may be effected almost as rapidly and uninterruptedly as under ordinary pressure.

X.—ON THE DECOMPOSITION OF ACETONE WITH BLEACHING POWDER.

By W. R. Orndorff and H. Jessel.

In the Annalen der Chemie, Vol. I, page 199, Liebig, after mentioning the formation of chloroform by distilling dilute alcohol with calcium hypochlorite, states that chloroform may also be obtained, and in greater quantity, if acetone be treated with calcium

[1] Ber. d. chem. Ges. **19**, R. 467.

hypochlorite, under the same circumstances. No other reference to the formation of chloroform from acetone occurs in the literature, if we except the statement of Siemerling[1] that the use of acetone for the preparation of chloroform is not advantageous, because the price of it is high and the product does not exceed one third of the acetone used. Notwithstanding Siemerling's statement, it has been found very advantageous to use acetone in the manufacture of chloroform, and at the present time a large amount of chloroform is actually made by the very method that Siemerling condemned. As there was nothing in the literature concerning the reaction which takes place when acetone is decomposed with bleaching powder, the present investigation was undertaken for the purpose of throwing some light on this subject.

The acetone used was a commercial product, boiling from 58° to 60° C. This was first dried over calcium chloride and then fractioned with a Hempel tube. The larger part of the acetone came over between 56° and 58° C., and this was used in all of the experiments. The bleaching powder was also a commercial article, and contained thirty-three and one third ($33\frac{1}{3}$) per cent. of available chlorine. The apparatus used consisted of a four-liter balloon flask provided with a three-hole rubber stopper. Through one of the holes passes a separatory funnel reaching to the bottom of the flask. The second hole has a glass tube of tolerably large diameter, which also reaches to the bottom of the flask. Through the third hole passes the exit tube, which is collected with a Liebig's condenser. The bleaching powder is placed in the flask together with the requisite amount of water. A weighed quantity of acetone, after having been diluted with a certain quantity of water, is then gradually added through the separatory funnel. The reaction begins spontaneously, and the chloroform distills without the application of external heat. After all the acetone has been added, and the heat of the reaction has somewhat subsided, the flask is placed on a water-bath and the bath heated. Steam is now passed through the mixture in the flask so as to drive out all the chloroform. The flask must be shaken while the acetone is being added, and care must be taken not to add the acetone too fast, otherwise the flask becomes very hot and the mass is apt to froth over, owing to the chloroform distilling too rapidly. After a long series of experiments the following proportions were found to

[1] Arch. for Pharm. Trier [2] **53,** 23.

give the best results: 275 grams of bleaching powder (33⅓ per cent. available chlorine) were mixed in the flask with 800 cc. of water ; 22 grams of acetone were then diluted with 70 cc. of water and gradually added through the separatory funnel. The yield of chloroform amounts to 166 to 173 per cent. of the weight of the acetone used. The chloroform obtained by this method was found to be very pure, and after being washed and dried, boiled constantly at 61.5°, and had the specific gravity 1.5263 as compared with water at 4°.

The residues left in the flask in a long series of experiments were united and filtered. The solid material left on the filter was examined and found to be almost entirely calcium hydroxide, together with a small amount of calcium hypochlorite and calcium carbonate. Through the clear filtrate carbon dioxide was passed to remove the calcium hydroxide in solution, then it was filtered and the filtrate treated with a concentrated solution of potassium carbonate as long as any calcium carbonate was precipitated. The precipitated calcium carbonate was then filtered off and the solution of the potassium salts evaporated to crystallisation. Two kinds of crystals were obtained, cubical crystals of potassium chloride, and needle-shaped crystals which appeared to be potassium acetate. Most of the potassium chloride was separated by fractional crystallisation from water. The mother-liquors were then evaporated to dryness on the water-bath and the dry mass treated with alcohol (95 per cent.), in which potassium acetate is very soluble and potassium chloride almost insoluble. The alcoholic solution was filtered and the filtrate evaporated to dryness on the water-bath. The dry mass was very deliquescent and absorbed moisture enough from the air to dissolve completely if allowed to stand unprotected. Treated with alcohol and sulphuric acid and distilled, acetic ether was formed. With a solution of ferric acetate it gave the characteristic precipitate of basic ferric acetate. A hot saturated solution, when treated with a strong solution of silver nitrate, filtered and allowed to cool, gave the characteristic flat needle-shaped crystals of silver acetate. These were separated, recrystallised from water, dried, and analysed with the following results :

	Found.	Calculated for $Ag(C_2H_3O_2)$.
	64.47	64.67
Ag	64.57	

26

From these results it will be seen that the products formed by the action of bleaching powder on acetone are chloroform, calcium hydroxide, calcium chloride, and calcium acetate.

It is probable that the first action of the bleaching powder is a substituting one, yielding trichloracetone or methyl chloral, according to the equation,

$$2CH_3COCH_3 + 6CaOCl_2 = 2CH_3COCCl_3 + 3Ca(OH)_2 + 3CaCl_2.$$
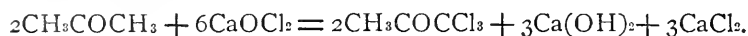
This methyl chloral is then acted on by the calcium hydroxide formed at the same time, and chloroform and calcium acetate are formed thus :

$$2CH_3COCCl_3 + Ca(OH)_2 = 2CHCl_3 + Ca(C_2H_3O_2)_2,$$
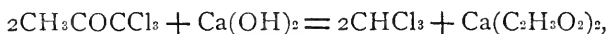
or, combining the two equations,

$$2CH_3COCH_3 + 6CaOCl_2 =$$
$$2CHCl_3 + 2Ca(OH)_2 + 3CaCl_2 + Ca(C_2H_3O_2)_2.$$
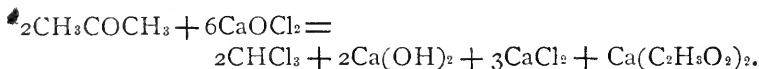
This equation requires for one molecule of acetone one of chloroform, or a yield of 206 per cent. of the weight of acetone used. The best yield obtained in the factory is 188 per cent. The amount of bleaching powder required by this equation agrees very well with the amount found by experiment to give the best results.

In the Annalen der Chemie, Vol. I, page 228, Liebig says that if acetone be warmed slightly with a solution of calcium hypochlorite, a strong precipitate of *calcium carbonate* is formed, and on distillation, chloroform passes over. As this statement is a direct contradiction of the above equation and the facts from which it was derived, a clear solution of bleaching powder was prepared by treating bleaching powder with water and filtering the solution, and then heated with a small quantity of acetone. A strong precipitate was thrown down at once, and the odor of chloroform was distinctly perceptible. The precipitate was filtered off and examined and found to be *calcium hydroxide*, and not *calcium carbonate* as stated by Liebig, thus confirming the results obtained above. Acetophenone ($C_6H_5COCH_3$), treated in the same way, caused the clear solution of bleaching powder to become clouded, owing to the precipitation of calcium hydroxide. On distillation, chloroform passed over, calcium benzoate was found in the flask from which the chloroform was distilled. In this case probably trichloracetophenone or phenyl chloral is first formed thus:

$$2C_6H_5COCH_3 + 6CaOCl_2 = 2C_6H_5COCCl_3 + 3Ca(OH)_2 + 3CaCl_2,$$
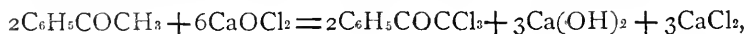
and this, with the calcium hydroxide formed at the same time, gives chloroform and calcium benzoate, thus :

$$2C_6H_5COCCl_3 + Ca(OH)_2 = (C_6H_5COO)_2Ca + 2CHCl_3.$$
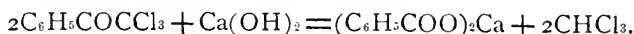
Bischoff[1] and Cloez[2] have shown that when acetone is treated with chlorine, trichloracetone or methyl chloral is the final product ; and both Krämer[3] and Morawski[4] have demonstrated that trichloracetone heated with a solution of an alkali yields chloroform. In order that there might be no doubt about this matter, acetone was treated with chlorine in the sunlight until it would absorb no more chlorine. The heavy oily product was then distilled with milk of lime, and chloroform was found in the distillate. Lieber[5] after giving a list of the substances which give the iodoform reaction when treated with iodine and caustic potash, states that all these bodies contain the methyl group, and that "man kann sich den Hergang bei der Reaction etwa so vorstellen, das KOH daran theilnimmt, indem H mit dem sich abspaltenden CH₃ und KO mit dem Rest in Verbindung tritt, während zugleich das Jod substituirend wirkt und so Jodoform bildet. Die Reaction findet nur dann statt wenn der vom CH₃ abgespaltene Rest geeignet ist, mit KO in Verbindung zu treten, d. h. entweder ein Säureradical ist, oder doch leicht sich durch Oxydation in ein solches verwandelt."

In the light of the results on the formation of chloroform from acetone and bleaching powder, it would seem that the formation of iodoform is in all respects analogous to the formation of chloroform, *i. e.* that the iodine first acts as a substituting agent, giving a tri-iodo substitution product, and that this breaks up in the presence of the alkali, yielding iodoform and an acid residue which unites with the caustic alkali. The above process of making chloroform from acetone might well be substituted for the one ordinarily given in text-books on organic chemistry, in which alcohol and bleaching powder are used. The yield of chloroform is much better, the process quicker and more satisfactory, and the explanation of the reaction, if anything, simpler.

[1] Ber. **8**, 1339.   [2] Ann. chim. phys. [6], **9**, 145.
[3] Ber. **7**, 258.   [4] J. prak. Chem. 1875, 388.
                    [5] Ann. Chem. Sp. Bd. **7**, 230.

XI.—ON THE DECOMPOSITION OF SOME DIAZO COMPOUNDS IN FORMIC AND ACETIC ACIDS.

By W. R. ORNDORFF.

The study of the decomposition of some of the simplest diazo compounds in formic acid was undertaken with the hope of realising the following equation :

$$C_6H_5N = N.NO_3 + HCOOH = C_6H_6 + N_2 + HNO_3 + CO_2.$$
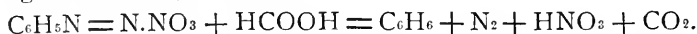
This reaction, if successful, would then furnish us with an easy means of replacing the amido group by hydrogen, and could be substituted for the decomposition of diazo compounds with alcohol, which has been shown not to be always reliable. It was soon found, however, that the reaction was of an entirely different character. No carbon dioxide was evolved, though decomposition took place readily and the N_2 group was driven out. Esters of formic acid seemed to have been formed, though it was impossible to prove this, owing to the fact that phenyl and cresyl formates decompose when distilled with steam or when heated to their boiling point. Since it was found impossible to isolate the first products of the decomposition of the diazo compounds with formic acid, acetic acid was substituted for formic acid.

Decomposition of diazo-benzene nitrate with glacial acetic acid.— The diazo-benzene nitrate was made according to the method of Griess, filtered off with the aid of the pump, washed with absolute alcohol and then with anhydrous ether, and finally spread out upon drying paper and allowed to remain until all the ether had evaporated. The white crystallised salt was then placed in a vacuum desiccator over sulphuric acid and allowed to remain until thoroughly dry. About 10 grams of the dry diazo-benzene nitrate were decomposed at a time. This quantity was placed in a liter Erlenmeyer flask and 100 cc. glacial acetic acid added. The flask was then placed in a water-bath and the bath heated. The diazo-benzene nitrate dissolved quite readily in the hot acetic acid and imparted to it a slightly yellowish red color. On continuing to heat until the water in the bath was about 70° C., nitrogen gas began to escape through the liquid. The lamp was then removed and the decomposition allowed to proceed. It was found that the decomposition was best effected at as low a temperature as possible, and if at any time the action became too violent it was

checked by dipping the flask in cold water. When the gas ceased to come off, the water in the bath was kept boiling for some time to insure the complete decomposition of all the diazo-benzene nitrate. The glacial acetic acid became deep red in color. The gas evolved was collected, examined, and found to be nitrogen. About 200 grams of the dry diazo-benzene nitrate were decomposed in this way in 10-gram portions. The portions of the red colored liquid left in the flask after each decomposition were poured together and the resulting liquid diluted with about ten times its bulk of water. A dark red colored oil separated out. After standing for some time this was collected, placed in a round-bottom flask with some water, and distilled in steam in order to free it from tarry impurities. It was then washed several times with a very dilute solution of sodium hydroxide, and finally dried over calcium chloride and subjected to fractional distillation. A colorless oil was obtained which boiled constantly at 195° C. (Anschütz thermometer, entirely in vapor ; bar. 733 mm.) On analysis this oil gave the following results :

	I.	II.	Calculated for $C_8H_8O_2$:
C	70.77	70.66	70.59
H	6.07	6.17	5.88

A small portion of the oil, when boiled with a strong solution of caustic potash, dissolved, and acetic acid and phenol were found to be present in this solution. These results show that the substance is undoubtedly phenyl acetate. The decomposition of diazo-benzene nitrate in glacial acetic acid therefore takes place in accordance with the equation,

$$C_6H_5N_2NO_3 + CH_3COOH = CH_3COOC_6H_5 + N_2 + HNO_3,$$
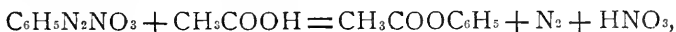
the products being phenyl acetate, nitrogen and nitric acid. This equation is analogous to that by which phenetol is formed by the action of alcohol on diazo-benzene nitrate,

$$C_6H_5N_2NO_3 + HOC_2H_5 = C_6H_5OC_2H_5 + N_2 + HNO_3.$$
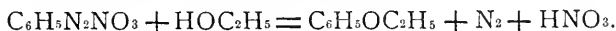
The yield of phenyl acetate is very small, owing to the fact that much tar is formed.

Phenyl Acetate.—This substance was first made by Cahours,[1] by the action of acetyl chloride on phenol. It has since been investigated by Scrugham,[2] Broughton,[3] Guareschi,[4] and by Perkin and Hodgkinson.[5] Different investigators have given it different boil-

[1] Ann. Chem. **92**, 316.   [2] Ann. Chem. **92**, 317.   [3] Ann. Chem. Spl. Bd. **4**, 121.
[4] Ann. Chem. **171**, 142.   [5] J. Chem. Soc. **37**, 487.

ing points, from 188° (Scrugham) to 200° (Broughton). Phenyl acetate was therefore made by treating pure phenol with a slight excess of acetyl chloride, heating the flask, connected with an air condenser, for some time until all the hydrochloric acid is driven off. The liquid remaining in the flask was then subjected to fractional distillation and the greater part was found to boil constantly at 195°. The thermometer used was an Anschütz standard thermometer and the mercury column was entirely surrounded by vapor. (Bar. 733 mm.) Phenyl acetate thus made is identical in all respects with that obtained by the decomposition of diazo-benzene nitrate with glacial acetic acid. It is a peculiar-smelling liquid, the odor lasting for some time. It is perfectly colorless when pure, and does not become colored on standing, provided it be perfectly pure (cf. Broughton). It is only very slightly soluble in water, to which it imparts its characteristic odor. It is soluble in ether, chloroform, alcohol, strong formic and glacial acetic acids. From the solution in formic and acetic acids it is precipitated on dilution with water. Benzene and petroleum ether dissolve it only when used in large excess. It is readily saponified when boiled with solutions of the caustic alkalies, forming acetates and phenolates. It is not decomposed by boiling water, and is readily volatile with steam. The specific gravity of phenyl acetate as determined by Broughton is 1.074. A determination of the specific gravity of the phenyl acetate made by the decomposition of diazobenzene nitrate in glacial acetic acid as well as of that made from phenol and acetyl chloride, using Perkin's modifications of the Sprengel specific gravity tube,[1] gave 1.0927 at 0° as compared with water at 4°C. One of the curious things about phenyl acetate is that its index of refraction being very nearly the same as that of German fusible glass, a piece of this is invisible when placed in the clear colorless fluid. This fact was first noted by Broughton.

Decomposition of p-diazo-toluene sulphate with glacial acetic acid.—*p*-Diazo-toluene sulphate was made and dried according to the method already given.[2] The perfectly dry white crystallised salt was then placed in a flask with glacial acetic acid and decomposed, using the same proportions, method, and precautions as in the case of the decomposition of diazo-benzene nitrate. Altogether about 300 grams were decomposed in 10-gram portions. The residues left in the flask were united and diluted with ten

[1] J. Chem. Soc. **45**, 444.   [2] Am. Chem. J. **9**, 387.

times the volume of water. The oil which separated out was then collected, distilled in steam to free it from impurities, washed two or three times with a very dilute solution of caustic soda, dried over calcium chloride and subjected to fractional distillation. A pleasant-smelling colorless oil was obtained which boiled constantly at 213° C. (Anschütz standard thermometer, entirely surrounded by vapor ; bar. 734 mm.) On analysis this oil gave the following results :

	I.	II.	Calculated for $C_9H_{10}O_2$.
C	72.14	71.92	72.00
H	6.67	6.68	6.66

It readily dissolved when boiled with a strong solution of caustic potash, and both para-cresol and acetic acid were found in this solution. A determination of the specific gravity with Perkin's specific gravity tube gave 1.0658 at 0° C. as compared with water at 4° C. From these results it will be seen that the reaction which takes place is represented by the equation

$$C_6H_4{<}^{CH_3}_{N_2HSO_4} + CH_3COOH = CH_3COOC_7H_7 + H_2SO_4 + N_2,$$
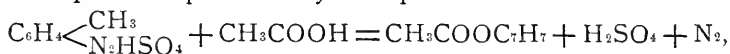
cresyl acetate, $CH_3COOC_7H_7$, being formed. The yield of cresyl acetate is very small, probably owing to some secondary reaction between the cresyl acetate and the sulphuric acid.

p-Cresyl Acetate.—This substance was first made by Fuchs,[1] and described by him as a yellow fluid having a disagreeable odor and boiling at 208°–211°. Perkin and Hodgkinson[2] also describe a cresyl acetate which they made by treating cresol (obtained from Kahlbaum) with acetyl chloride. This, they say, is a beautiful colorless fluid, boiling at 214° ; but as they do not state whether their cresol was the ortho, meta, or para compound, it is impossible to say whether their cresyl acetate was identical with that of Fuchs or not. Fuchs used the para-cresol, and therefore his cresyl acetate was undoubtedly the para compound. In order to determine accurately the boiling point and properties of *p*-cresyl acetate, and to compare it with the substance obtained by the decomposition of *p*-diazo-toluene sulphate with glacial acetic acid, pure *p*-cresol (m. p. 36°) was treated with a slight excess of acetyl chloride, and heated in a flask connected with an air condenser until all the hydrochloric acid was driven off. The liquid was then subjected to fractional distillation, and the larger part was found

[1] Ber. **2,** 626.　　[2] J. Chem. Soc. **37,** 489.

to boil constantly at 213°. (Anschütz thermometer, entirely surrounded by vapor; bar. 734 mm.) Thus made, cresyl acetate is a colorless oil, highly refracting, having a pleasant odor when pure, but an exceedingly disagreeable one in the impure state. It is but slightly soluble in water, and readily volatilises with steam without undergoing any decomposition. It is soluble in alcohol, ether, chloroform, in formic and acetic acids, and in large excess of benzene and petroleum ether. From its solution in formic and acetic acids it is precipitated on dilution with water. The specific gravity of the *p*-cresyl acetate made from *p*-cresol and acetyl chloride was determined very accurately by means of a specific gravity U tube (Perkin's modification of Sprengel's sp. gr. tube), and found to be the same as that already determined for the *p*-cresyl acetate made by the decomposition of *p*-diazo-toluene sulphate with glacial acetic acid, viz. 1.0657 at 0° C. compared with water at 4° C. From these results it will be seen that the cresyl acetates from the two sources are undoubtedly identical.

The *p*-diazo-benzene-sulphonic acid of Schmitt[1] was made according to the method of Fischer[2] and decomposed in glacial acetic acid. Much nitrogen was evolved and the liquid became colored a deep red. After evaporating off all the acetic acid on the water-bath, a syrupy liquid remained which had acid properties and appeared to be the *p*-acetyl-phenol-sulphonic acid, $C_6H_4{<}{OOCCH_3 \atop SO_3H}$. Owing to lack of time nothing further was done with this compound. Meldola[3] has recently shown that the same reaction takes place in the naphthalene group. He obtained *m*-nitro-benzene-azo-acetyl-β-naphthol by treating *m*-nitro-benzene-azo-β-naphthylamine with glacial acetic acid and sodium nitrite. It may therefore be assumed that the reaction between diazo compounds and glacial acetic acid is a general one for all diazo compounds. The only other reference to such a reaction in the literature is a statement of Hayduck[4] that when diazo-*o*-amido-*p*-toluene-sulphonic acid, $C_6H_3{\left\{ {CH_3 \atop {N_2 \atop SO_2}}{>} \right.}$ was decomposed with glacial acetic acid, it gave an acid containing the acetyl group and which formed crystallisable salts with bases. The reaction, however, he says, is not simple, and here he leaves the work.

[1] Ann. Chem. **120**, 144.   [2] Ann. Chem. **190**, 76.
[3] Ber. **21**, 601. When Meldola published his preliminary notice in the Berichte, the work described in this paper was nearly completed.   [4] Ann. **172**, 217.

LXI.—ON SUBSTITUTED PYROMUCIC ACIDS.

SECOND PAPER.

By Henry B. Hill and Arthur W. Palmer.[1]

On Sulphopyromucic Acids.[2]

Pyromucic acid shows in many of its reactions so close an analogy to benzoic acid that a study of its behavior toward concentrated sulphuric acid could hardly fail to yield interesting results. In 1860 Schwanert[3] prepared a sulphopyromucic acid by distilling sulphuric anhydride slowly over powdered pyromucic acid. The barium salt was said to be not distinctly crystalline, and its composition was established by a single determination of barium in the salt dried at 150°. With the exception of the brief notice by Schwanert, we have been able to find no mention of furfuran derivatives containing the sulpho group. We have found that a sulphopyromucic acid is formed without difficulty when pyromucic acid is dissolved in fuming sulphuric acid, and that a second sulphonic acid may readily be made by indirect methods. We have also prepared and studied several derivatives of these sulphonic acids containing bromine, and have succeeded in establishing the constitution of these various products.

δ-*Sulphopyromucic Acid.*

If dry pyromucic acid is slowly added to fuming sulphuric acid (sp. gr. 1.95), it dissolves without serious discoloration, and in a short time the formation of the sulphonic acid is complete. We have usually taken three parts of sulphuric acid to one of pyromucic, and have allowed the viscous solution to stand for twenty-four hours before diluting and neutralising with baric carbonate. The aqueous solution filtered from the baric sulphate and concentrated by evaporation deposits on cooling globular aggregations of minute crystals which are readily purified by recrystallisation

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[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] A part of the work described in the following paper was presented in the form of a thesis to the Academic Council of Harvard University in May, 1886, by Arthur W. Palmer, then candidate for the degree of Doctor of Science.

[3] Ann. Chem. (Liebig), **116**, 268.

from hot water. The acid prepared by exact precipitation with sulphuric acid is extremely soluble in water, but may be obtained by concentration in large transparent prisms which deliquesce in moist air.

Baric δ-Sulphopyromucate, $BaC_5H_2SO_6.4H_2O$.—This salt crystallises in thin flat prisms which are usually closely aggregated in hemispherical masses. It is readily soluble in hot water, more sparingly soluble in cold water, and its aqueous solution is precipitated by the addition of alcohol. When dried by exposure to the air it contains four molecules of water, a part of which it slowly loses over sulphuric acid or at $100°$, the rest at $160°$.

I. 2.1205 grams of the air-dried salt lost, at $162°$, 0.3827 gram H_2O.

II. 2.5754 grams of the air-dried salt lost, at $160°$, 0.4605 gram H_2O.

	Calculated for $BaC_5H_2SO_6.4H_2O$.	Found. I.	II.
H_2O	18.02	18.05	17.88

I. 0.7695 gram of the salt dried at $160°$ gave 0.5480 gram $BaSO_4$.

II. 0.7010 gram of the salt dried at $160°$ gave 0.4990 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_6$.	Found. I.	II.
Ba	41.90	41.87	41.85

The solubility of the salt in cold water we have determined according to the method of V. Meyer.

I. 15.1350 grams of a solution saturated at $21°$ gave 0.3672 gram $BaSO_4$.

II. 13.9856 grams of a solution saturated at $21°$ gave 0.3384 gram $BaSO_4$.

The aqueous solution saturated at $21°$ therefore contained the following percentages of the anhydrous salt:

I.	II.
3.40	3.39

Acid Baric δ-Sulphopyromucate, $Ba(C_5H_3SO_6)_2.4H_2O$ and $6H_2O$.—Although this salt may be formed by the action of hydrochloric acid upon the neutral salt, its ready solubility in cold water makes it more conveniently prepared from equivalent quantities of the free acid and the neutral salt. On cooling the concentrated

solution, the salt separates in long slender prisms containing six molecules of water. From more dilute solutions, when crystallisation begins at ordinary temperatures, the salt separates in well formed rhombic plates which contain four molecules of water. Not unfrequently both forms appear together, and we have not been able to determine with precision the conditions essential to the formation of either. The long slender prisms effloresce slowly when exposed to the air. When dried by pressure and by short exposure to the air, it gave the following results :

I. 0.6298 gram of the salt lost, at 100°, 0.1056 gram H_2O.

II. 1.7845 gram of the salt lost, at 120°, 0.3055 gram H_2O.

	Calculated for $Ba(C_5H_3SO_6)_2.6H_2O$.	I.	Found. II.
H_2O	17.22	16.77	17.12

I. 0.5242 gram of the salt dried at 100° gave 0.2361 gram $BaSO_4$.

II. 0.7035 gram of the salt dried at 120° gave 0.3155 gram $BaSO_4$.

III. 0.7629 gram of the salt dried at 120° gave 0.3420 gram $BaSO_4$.

	Calculated for $Ba(C_5H_3SO_6)_2$.	I.	Found. II.	III.
Ba	26.39	26.48	26.36	26.35

The rhombic plates did not lose in weight when exposed to the air, and but slowly over sulphuric acid. The air-dried salt gave the following results :

I. 4.3735 grams of the air-dried salt lost, at 105°, 0.5235 gram H_2O.

II. 1.4496 gram of the air-dried salt lost, at 105°, 0.1762 gram H_2O.

III. 1.6332 gram of the air-dried salt lost, at 135°, 0.2010 gram H_2O.

	Calculated for $Ba(C_5H_3SO_6)_2.4H_2O$.	I.	Found. II.	III.
H_2O	12.18	11.97	12.16	12.31

I. 0.6969 gram of the salt dried at 105° gave 0.3125 gram $BaSO_4$.

II. 0.6325 gram of the salt dried at 140° gave 0.2825 gram $BaSO_4$.

III. 0.5982 gram of the salt dried at 140° gave 0.2682 gram $BaSO_4$.

	Calculated for $Ba(C_5H_3SO_6)_2$.	I.	Found. II.	III.
Ba	26.39	26.36	26.26	26.36

Calcic δ-Sulphopyromucate, $CaC_5H_2SO_6.3H_2O$.—This salt is quite soluble in cold water, and crystallises in flat concentrically grouped prisms which slowly effloresce over sulphuric acid.

0.7413 gram of the salt lost, at 130°, 0.1364 gram H_2O.

	Calculated for $CaC_5H_2SO_6.3H_2O$.	Found.
H_2O	19.01	18.40

I. 0.5737 gram of the salt dried at 125° gave 0.3383 gram $CaSO_4$.

II. 0.6405 gram of the salt dried at 125° gave 0.3770 gram $CaSO_4$.

	Calculated for $CaC_5H_2SO_6$.	Found. I.	II.
Ca	17.40	17.34	17.31

Plumbic δ-Sulphopyromucate, $PbC_5H_2SO_6.2H_2O$.—This salt is readily soluble in hot water, more sparingly in cold, and crystallises in clustered needles. The air-dried salt contained two molecules of water.

2.1320 grams of the air-dried salt lost at 105° 0.1805 gram H_2O.

	Calculated for $PbC_5H_2SO_6.2H_2O$.	Found.
H_2O	8.31	8.47

I. 0.6682 gram of the salt dried at 110° gave 0.5085 gram $PbSO_4$.

II. 0.5046 gram of the salt dried at 110° gave 0.3837 gram $PbSO_4$.

III. 1.0150 gram of the salt dried at 110° gave 0.5570 gram CO_2 and 0.0660 gram H_2O.

	Calculated for $PbC_5H_2SO_6$.	I.	Found. II.	III.
Pb	52.14	51.99	51.96	
C	15.16	...	...	14.97
H	0.50	...	...	0.72

Argentic δ-Sulphopyromucate, $Ag_2C_5H_2SO_6$.—The silver salt is sparingly soluble in cold water, somewhat more readily soluble in hot water, and crystallises in short thick prisms. The air-dried salt lost slightly in weight when heated at 120°, but the loss was insignificant.

I. 0.6788 gram of the salt gave 0.4779 gram AgCl and 0.3923 gram $BaSO_4$.

II. 0.5255 gram of the salt gave 0.3703 gram AgCl and 0.3028 gram $BaSO_4$.

	Calculated for $Ag_2C_5H_2SO_6$.	Found. I.	II.
Ag	53.21	53.01	53.04
SO_3	19.97	19.85	19.78

Potassic δ-Sulphopyromucate, $K_2C_5H_2SO_6.4H_2O$.—The potassium salt is extremely soluble even in cold water, and crystallises in long slender prisms which apparently contain four molecules of water. They effloresce quite rapidly when exposed to the air, and our determinations of the water of crystallisation are, therefore, not entirely satisfactory.

I. 2.4108 grams of the salt dried by short exposure to the air lost, at 135°, 0.4966 gram H_2O.

II. 0.9701 gram of the salt dried by pressure only lost, at 100°, 0.2074 gram H_2O.

III. 1.3420 gram of the salt dried by short exposure to the air lost, at 115°, 0.2775 gram H_2O.

	Calculated for $K_2C_5H_2SO_6.4H_2O$.	I.	Found. II.	III.
H_2O	21.15	20.60	21.38	20.68

I. 0.5573 gram of the anhydrous salt gave 0.3608 gram K_2SO_4.

II. 0.5035 gram of the anhydrous salt gave 0.3242 gram K_2SO_4.

	Calculated for $K_2C_5H_2SO_6$.	I.	Found. II.
K	29.16	29.07	28.91

Acid Potassic δ-Sulphopyromucate, $KC_5H_3SO_6$.—The acid potassium salt is very soluble in water, and crystallises in large anhydrous prisms.

I. 0.8655 gram of the salt gave 0.3253 gram K_2SO_4.

II. 0.8290 gram of the salt gave 0.3127 gram K_2SO_4.

III. 0.7694 gram of the salt gave 0.2879 gram K_2SO_4.

	Calculated for $KC_5H_3SO_6$.	I.	Found. II.	III.
K	16.99	16.89	16.93	16.81

Sodic δ-Sulphopyromucate, $Na_2C_5H_2SO_6.5H_2O$.—The neutral sodium salt is extremely soluble in water, and crystallises in long slender needles which appear to contain five molecules of water.

The same salt is obtained in the form of fine felted needles by crystallisation from dilute alcohol.

I. 1.5082 gram of the salt dried by short exposure to the air lost, at 110°, 0.3970 gram H_2O.

II. 1.4198 gram of the salt recrystallised from dilute alcohol and dried by short exposure to the air lost, at 135°, 0.3773 gram H_2O.

III. 1.0232 gram of the salt recrystallised from dilute alcohol and dried by pressure only, lost, at 135°, 0.2785 gram H_2O.

	Calculated for $Na_2C_5H_2SO_6.5H_2O$.	I.	Found. II.	III.
H_2O	27.61	26.32	26.57	27.22

I. 0.5195 gram of the salt dried at 110° gave 0.3115 gram Na_2SO_4.

II. 0.5592 gram of the salt dried at 110° gave 0.3357 gram Na_2SO_4.

	Calculated for $Na_2C_5H_2SO_6$.	I.	Found. II.
Na	19.49	19.43	19 45

Acid Sodic δ-Sulphopyromucate, $NaC_5H_3SO_6.H_2O$.—This salt crystallises in long slender prisms which do not lose in weight when exposed to the air or over sulphuric acid.

I. 2.1303 grams of the air-dried salt lost, at 110°, 0.1658 gram H_2O.

	Calculated for $NaC_5H_3SO_6.H_2O$.	Found.
H_2O	7.76	7.78

I. 1.0224 gram of the salt dried at 110° gave 0.3371 gram Na_2SO_4.

II. 0.9498 gram of the salt dried at 110° gave 0.3154 gram Na_2SO_4.

	Calculated for $NaC_5H_3SO_6$.	I.	Found. II.
Na	10.75	10.69	10.76

δ-Sulphopyromucamide, $C_5H_2SO_4(NH_2)_2$.—By acting upon the dry sodium salt of δ-sulphopyromucic acid with phosphoric pentachloride, and expelling at a gentle heat the greater part of the phosphoric oxychloride formed in the reaction, a viscous oil was obtained which did not invite further investigation. It was, therefore, at once converted into the corresponding amide by the action of concentrated ammonic hydrate. The product of the reaction, after recrystallisation from boiling water, formed long flat prisms

readily soluble in hot water, sparingly soluble in cold water, which melted at 213°.

I. 0.3441 gram of substance gave 47.2 cc. moist nitrogen at 27° and under a pressure of 763 mm.

II. 0.2025 gram of substance gave 0.2507 gram $BaSO_4$.

	Calculated for $C_5H_2SO_4(NH_2)_2$.	I.	Found. II.
N	14.73	15.18	
S	16.84	...	17.00

Action of Bromine.

At ordinary temperatures dry bromine has little or no action upon dry δ-sulphopyromucic acid. At 100° in a sealed tube a complicated reaction ensues which we have not yet fully investigated. Ordinary dibromsuccinic acid is formed in considerable quantity, and at the same time a small amount of mucobromyl bromide, as was shown by the blue color developed in alkaline solution, and by the formation of mucobromic acid melting at 120°–121° on heating with water. There was also formed in small quantity a beautifully crystalline substance, sparingly soluble even in boiling alcohol, which contained sulphur but no bromine. This substance we unfortunately have not yet succeeded in obtaining in quantity sufficient for further study.

In aqueous solution bromine rapidly oxidises δ-sulphopyromucic acid, even in the cold. The final product of the reaction is fumaric acid, and we have hitherto been unable to isolate any intermediate products. It is probable, however, that maleic acid is in fact the first product of the oxidation. If bromine be added to an aqueous solution of the barium salt of the acid, baric sulphate is immediately thrown down ; but since the amount of baric sulphate thus formed is slightly less than the theoretical quantity, secondary products containing sulphur are doubtless formed. In the complete oxidation of the acid we have used a slight excess of bromine, and have finished the reaction by gentle heat. The fumaric acid obtained was identified by qualitative tests and by the analysis of the silver salt.

I. 0.2124 gram of the salt dried at 120° gave 0.2406 gram $AgBr$.

II. 0.2056 gram of the salt dried at 120° gave 0.2332 gram $AgBr$.

	Calculated for $Ag_2C_4H_2O_4$.	I.	Found. II.
Ag	65.46	65.07	65.15

The decomposition with bromine, therefore, takes place in great part according to the equation,

$$C_5H_4SO_6 + 3Br_2 + 4H_2O = C_4H_4O_4 + CO_2 + H_2SO_4 + 6HBr.$$
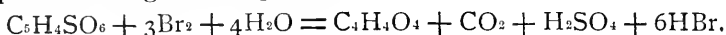
Action of Nitric Acid.

The oxidation of δ-sulphopyromucic acid with dilute nitric acid takes place but slowly, and even after long boiling with moderately concentrated acid the decomposition is far from complete.   After boiling for some time with acid of sp. gr. 1.20 and evaporation upon the water-bath, fumaric acid was obtained, together with small quantities of oxalic acid.   The fumaric acid was identified, as before, by its physical properties and by analysis of its silver salt.

0.1508 gram of the salt dried at 125° gave 0.1710 gram AgBr.

	Calculated for $Ag_2C_4H_2O_4$.	Found.
Ag	65 46	65.15

The reaction with concentrated nitric acid is much more inter-esting, since the sulpho group is in this way replaced by the nitro group and the δ-nitropyromucic acid of Klinkhardt,[1] formed with comparatively little oxidation.   This replacement is slowly effected at ordinary temperatures, but rapidly at 100°.   Dry sulphopyro-mucic acid is slowly added to several times its weight of cold fuming nitric acid.   The mixture is at first cooled, and the reaction afterward completed by gentle heat.   The nitric acid is then par-tially removed by evaporation, and the nitropyromucic acid, which separates as the solution cools, recrystallised from hot water.   For its complete purification we found it necessary to dissolve the acid in a cold dilute solution of sodic carbonate, to extract with ether this alkaline solution, and to recrystallise from hot water the product obtained by the addition of hydrochloric acid.   The pale yellow acid thus obtained crystallised in rectangular plates which melted at 182°–183°.

0.4925 gram substance gave 37.9 cc. of moist nitrogen at 16° and under a pressure of 748 mm.

	Calculated for $C_5H_3(NO)_2O_3$.	Found.
N	8.91	8.82

The ethyl ether of the acid was easily formed by warming its alcoholic solution with concentrated sulphuric acid.   It was spar-

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[1] J. prak. Chem. N. F. **25**, 41.

ingly soluble in cold alcohol, and crystallised in broad lustrous plates which melted at 99°–100°. Klinkhardt gives the melting point of the acid as 183°, and of the ether as 101°.

With the δ-nitropyromucic acid is formed in small quantity a neutral substance containing nitrogen, which was obtained by evaporating the ether used in the extraction of the alkaline solution of the crude nitropyromucic acid. The same substance was formed in somewhat larger quantity when we attempted to prepare nitropyromucic acid without isolating the sulphonic acid by the addition of nitric acid to a solution of pyromucic acid in fuming sulphuric acid. The substance dissolved sparingly in boiling water, and crystallised on cooling in clustered prisms which melted at 100°–101°. On warming with sodic hydrate a bright yellow color was developed. A filter paper moistened with its alcoholic solution and exposed to the vapors of ammonic sulphide turned yellow at first, then salmon-red. This behavior corresponds closely with that observed by V. Meyer[1] and Otto Stadler in the case of nitro derivatives of thiophen. Although from lack of material we have as yet made no analyses of this substance, we shall describe later a dibromdinitrofurfuran,[2] which was obtained under similar conditions from the βγ-dibrom-δ-sulphopyromucic acid, whose formation leaves no doubt that this substance is in fact αα-dinitrofurfuran. It will be further studied in the future in this laboratory.

Fusing potassic hydrate converts the δ-sulphopyromucic acid into succinic acid, and at the same time more or less oxalic acid is formed. Although we have also made certain experiments concerning the action of fusing sodic formiate, we have as yet reached no satisfactory conclusion, and must therefore postpone all consideration of our results until we have made further investigations.

β-Brom-δ-Sulphopyromucic Acid.

Although we have not succeeded in preparing substitution products directly from δ-sulphopyromucic acid, they may readily be made by the action of fuming sulphuric acid upon substituted pyromucic acids. If β-brompyromucic acid is dissolved in three times its weight of fuming sulphuric acid (sp. gr. 1.95), no carbonisation takes place at ordinary temperatures, and from the diluted solution may be isolated by neutralisation with baric carbonate the barium

[1] Ber. d. chem. Ges. **17**, 2779.   [2] Page 391.

salt of β-brom-δ-sulphopyromucic acid. The free acid is extremely soluble even in cold water, and crystallises in radiating needles which deliquesce rapidly in moist air.

Baric β-Brom-δ-Sulphopyromucate, $BaC_5HBrSO_6.4H_2O$.— This salt is readily soluble in hot water, more sparingly soluble in cold water, and crystallises in flat clustered prisms. It is precipitated in the form of fine needles on the addition of alcohol to its aqueous solution. The air-dried salt contains four molecules of water, most of which it loses over sulphuric acid, the rest at 100°.

I. 1.9130 gram of the air-dried salt lost, at 100°, 0.2824 gram H_2O.

II. 1.1010 gram of the air-dried salt lost, at 170°, 0.1630 gram H_2O.

	Calculated for $BaC_5HBrSO_6.4H_2O$.	Found. I.	Found. II.
H_2O	15.06	14.76	14.80

I. 0.3030 gram of the salt dried at 170° gave 0.1740 gram $BaSO_4$.

II. 0.3293 gram of the salt dried at 170° gave 0.1886 gram $BaSO_4$.

	Calculated for BaC_5HBrSO_6.	Found. I.	Found. II.
Ba	33.75	33.76	33.67

The solubility of the salt in cold water we determined according to the method of V. Meyer.

I. 27.6020 grams of the solution saturated at 21° gave 0.2300 gram $BaSO_4$.

II. 27.9011 grams of the solution saturated at 21° gave 0.2369 gram $BaSO_4$.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt:

I.	II.
1.45	1.48

Calcic β-Brom-δ-Sulphopyromucate, $CaC_5HBrSO_6.6H_2O$.—The calcium salt proved to be extremely soluble even in cold water. The syrupy solution gradually solidified, with the separation of long radiating needles. The air-dried salt apparently contained six molecules of water, five of which it rapidly lost over sulphuric acid.

I. 1.2305 gram of the air-dried salt lost, at 135°, 0.3193 gram H_2O.

II. 0.4444 gram of the air-dried salt gave 0.1413 gram $CaSO_4$.

	Calculated for $CaC_5HBrSO_6.6H_2O$.	I.	Found.	II.
H_2O	25.90	25.95		...
Ca	9.59	...		9.35

0.9631 gram of the salt dried over sulphuric acid lost, at 135°, 0.0519 gram H_2O.

	Calculated for $CaC_5HBrSO_6.H_2O$.	Found.
H_2O	5.51	5.39

0.4608 gram of the salt dried at 135° gave 0.1973 gram $CaSO_4$.

	Calculated for CaC_5HBrSO_6.	Found.
Ca	12.94	12.60

Plumbic β-Brom-δ-Sulphopyromucate, $PbC_5HBrSO_6.4H_2O$.— The lead salt is freely soluble in hot water, more sparingly in cold water, and crystallises in flat clustered prisms, or on rapid cooling in clustered needles. The air-dried salt contains four molecules of water, almost the whole of which it rapidly loses over sulphuric acid.

I. 1.3814 gram of the air-dried salt lost, at 130°, 0.1758 gram H_2O.

II. 1.9209 gram of the air-dried salt lost, at 140°, 0.2507 gram H_2O.

III. 0.3442 gram of the air-dried salt gave 0.1905 gram $PbSO_4$.

IV. 0.6382 gram of the air-dried salt gave 0.3530 gram $PbSO_4$.

	Calculated for $PbC_5HBrSO_6.4H_2O$.	I.	II.	Found. III.	IV.
H_2O	13.14	12.73	13.05	...	...
Pb	37.78	...	...	37.80	37.79

Potassic β-Brom-δ-Sulphopyromucate, $K_2C_5HBrSO_6.1\frac{1}{2}H_2O$ (?). —This salt is readily soluble in cold water, more sparingly soluble in dilute alcohol. It crystallises in small six-sided plates which are permanent in the air, but which effloresce over sulphuric acid. Two determinations of the water of crystallisation made in different preparations agree precisely with each other, but do not correspond well with any simple formula for the salt.

I. 0.8184 gram of the air-dried salt lost, at 160°, 0.0537 gram H_2O.

II. 1.4398 gram of the air-dried salt lost, at 160°, 0.0942 gram H_2O.

	Calculated for $K_2C_5HBrSO_6.H_2O.$	Calculated for $K_2C_5HBrSO_6.1\frac{1}{2}H_2O.$	Found. I.	II.
H_2O	4.93	7.22	6.56	6.55

0.3652 gram of the salt dried at 160° gave 0.1825 gram K_2SO_4.

	Calculated for $K_2C_5HBrSO_6.$	Found.
K	22.52	22.44

The connection between this brom-sulphopyromucic acid and the δ-sulphopyromucic acid could evidently be proved most neatly and directly by eliminating from it the bromine and examining carefully the sulphonic acid thus formed. By warming a strongly ammoniacal solution of the barium salt with zinc dust the bromine was quickly removed. The filtered solution was boiled with a slight excess of baric hydrate until all the ammonia was expelled and the zinc precipitated. The solution was then freed from the excess of baric hydrate by means of carbonic dioxide, and concentrated on the water-bath. On cooling, the solution deposited globular aggregations of colorless crystals which appeared to be identical with those of baric δ-sulphopyromucate. The identity was fully established by analyses of the salt, and by determinations of its solubility in water.

I. 1.5700 gram of the air-dried salt lost, at 165°, 0.2803 gram H_2O.

II. 0.7309 gram of the air-dried salt gave 0.4295 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_6.4H_2O.$	Found. I.	II.
H_2O	18.02	17.85	...
Ba	34.34	...	34.55

0.4947 gram of the salt dried at 165° gave 0.3505 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_6.$	Found.
Ba	41.90	41.67

I. 12.0595 grams of the solution saturated at 21° gave 0.2985 gram $BaSO_4$.

II. 12.1863 grams of the solution saturated at 21° gave 0.2989 gram $BaSO_4$.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt:

I.	II.
3.47	3.44

These results are sufficient to prove that the sulphonic acid formed by the reduction of the β-brom-δ-sulphopyromucic acid is identical with that obtained directly from pyromucic acid by the action of sulphuric acid.

Action of Bromine.

Bromine in aqueous solution readily oxidises β-brom-δ-sulpho-pyromucic acid or its salts. Since the relative position of the bromine and the sulpho group had already been established, we thought it necessary to do no more than identify the final product of the oxidation. Bromine was added in slight excess to an aqueous solution of the barium salt, and the reaction completed at a gentle heat. The strongly acid solution was filtered from the baric sulphate which had been formed, and extracted with ether. The ether left on evaporation a white crystalline acid which softened somewhat at 120° and melted completely at 165°. After two recrystallisations from water the acid melted sharply at 176°–177°, and was therefore monobromfumaric acid. The oxidation took place according to the following equation :

$$C_5H_3BrSO_6 + 3Br_2 + 4H_2O = C_4H_3BrO_4 + CO_2 + H_2SO_4 + 6HBr.$$
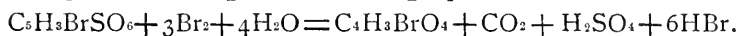
Action of Nitric Acid.

We have made no experiments concerning the action of dilute nitric acid upon β-brom-δ-sulphopyromucic acid, since it could safely be assumed that oxidation would ensue as with the δ-sulpho-pyromucic acid, and that monobromfumaric acid would be formed. It seemed to us, however, of decided interest to act upon the acid with fuming nitric acid, since a bromnitropyromucic acid should then result. Dry β-brom-δ-sulphopyromucic acid was slowly added to three times its weight of fuming nitric acid. The reaction progressed slowly in the cold, more rapidly on warming, and without any considerable oxidation. After the reaction was completed, the greater part of the nitric acid was expelled by gentle heat, the crystalline acid left was dissolved in a dilute solution of sodic carbonate, and the alkaline solution then extracted with ether. Upon evaporation of the ether a small quantity of a neutral oil was left, which gradually solidified. The quantity of the product which we thus obtained was so minute that further investigation was out of the question. The alkaline solution when acidified and again extracted with ether yielded in abundance a crystalline acid which

proved to be β-brom-δ-nitropyromucic acid. It was readily soluble in alcohol, ether, or hot benzol, more sparingly in cold benzol. It dissolved freely in hot water, and as the solution cooled it was deposited in long clustered flattened needles which contained one molecule of water. The anhydrous acid melted at 159°–160°. At 100° the acid appeared to sublime slowly.

I. 1.2492 gram of the acid crystallised from water lost, at 60°, 0.0911 gram H_2O.[1]

II. 0.9980 gram of the acid crystallised from water lost, at 78°, 0.0740 gram H_2O.

	Calculated for $C_5H_2Br(NO_2)O_3.H_2O$.	Found. I.	II.
H_2O	7.09	7.29	7.42

I. 0.2065 gram of the acid dried at 100° gave 0.1652 gram $AgBr$.

II. 0.2648 gram of the acid dried at 100° gave 14.2 cc. of moist nitrogen at 20° and under a pressure of 763 mm.

	Calculated for $C_5H_2Br(NO_2)O_3$.	Found. I.	II.
Br	33.90	34.04	...
N	5.93	...	6.15

This acid will be further studied in this laboratory. There can be no doubt, however, that, like the nitropyromucic acid of Klinkhardt, it contains the nitro group in the δ position.

$\beta\gamma$-Dibrom-δ-Sulphopyromucic Acid.

$\beta\gamma$-dibrompyromucic acid dissolves in fuming sulphuric acid without the slightest carbonisation, and is converted in a short time into the corresponding sulphonic acid. A large part of our work was done with material made from pure $\beta\gamma$-dibrompyromucic acid. We subsequently found, however, as will be described more at length later in this paper, that the $\beta\delta$-dibrompyromucic was but little affected by fuming sulphuric acid if the action were not too long continued, and that the mixture of the isomeric dibrompyromucic acids obtained from pyromucic tetrabromide could therefore advantageously be employed direct. The mixed acids were dissolved in once and a half their weight of fuming sulphuric acid, and the solution diluted with water after the lapse of two or three hours. The $\beta\delta$-dibrompyromucic acid thus precipitated was removed by filtration, and the solution neutralised as usual by

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[1] A slight mechanical loss renders the result of this determination uncertain in the second decimal place.

baric carbonate. The small amount of $\beta\delta$-dibrompyromucic acid, or its decomposition products, which remained in solution, could readily be removed by the recrystallisation of the barium salt which was obtained after evaporation. Since the separation of the isomeric dibrompyromucic acids is a matter of some difficulty, the preparation of the sulphonic acid in question is thus greatly facilitated. The free acid is very soluble even in cold water, but is more sparingly soluble in ordinary concentrated sulphuric acid. From sulphuric acid it crystallises in clustered needles, from water it is deposited in broad flat prisms which are permanent under ordinary atmospheric conditions.

Baric $\beta\gamma$-Dibrom-δ-Sulphopyromucate, $BaC_5Br_2SO_6.5H_2O$.— This salt is very readily soluble in hot water, more sparingly in cold water. The hot saturated solution solidifies on cooling, with the separation of long silky radiating needles. The air-dried salt contains five molecules of water, a part of which it loses over sulphuric acid.

I. 1.5136 gram of the air-dried salt lost, at 125°, 0.2422 gram H_2O.

II. 1.7684 gram of the air-dried salt lost, at 160°, 0.2855 gram H_2O.

III. 2.5118 grams of the air-dried salt lost, at 180°, 0.4013 gram H_2O.

	Calculated for $BaC_5Br_2SO_6.5H_2O$.	I.	Found. II.	III.
H_2O	15.65	16.01	16.14	15.97

I. 0.5378 gram of the salt dried at 125° gave 0.2575 gram $BaSO_4$.

II. 0.4688 gram of the salt dried at 180° gave 0.2243 gram $BaSO_4$.

III. 0.5317 gram of the salt dried at 180° gave 0.2550 gram $BaSO_4$.

	Calculated for $BaC_5Br_2SO_6$.	I.	Found. II.	III.
Ba	28.25	28.15	28.13	28.19

The solubility of the salt in cold water we determined in the usual way.

I. 10.9011 grams of the solution saturated at 20° gave 0.2170 gram $BaSO_4$.

II. 11.9609 grams of the solution saturated at 20° gave 0.2398 gram $BaSO_4$.

The solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt:

I.	II.
4.14	4.17

When an aqueous solution of the barium salt is evaporated at 100°, small clear prisms separate, which contain less water than the salt just described. We found it impossible to prepare this salt satisfactorily for analysis, since it at once took up water in the cold. A preparation which was removed from the hot solution and immediately dried by pressure with filter paper gave on analysis the following results:

I. 1.6161 gram of the salt lost, at 140°, 0.1767 gram H_2O.

II. 0.6265 gram of the salt gave 0.2665 gram $BaSO_4$.

	Calculated for $BaC_5Br_2SO_6.3H_2O$.	I.	Found. II.
H_2O	10.02	10.93	...
Ba	25.42	...	25.01

Plumbic βγ-Dibrom-δ-Sulphopyromucate, $PbC_5Br_2SO_6 \, 4H_2O$.—
The lead salt is readily soluble in hot water, more sparingly in cold, and crystallises in fine felted needles which are permanent in the air, but effloresce over sulphuric acid.

I. 1.4993 gram of the air-dried salt lost, at 165°, 0.1686 gram H_2O.

II. 1.0386 gram of the air-dried salt lost, at 165°, 0.1159 gram H_2O.

III. 0.6246 gram of the air-dried salt gave 0.3015 gram $PbSO_4$.

	Calculated for $PbC_5Br_2SO_6 \, 4H_2O$.	I.	Found. II.	III.
H_2O	11.48	11.24	11.16	...
Pb	33.01	...	...	32.98

0.5019 gram of the salt dried at 165° gave 0.2741 gram $PbSO_4$.

	Calculated for $PbC_5Br_2SO_6$.	Found.
Pb	37.32	37.32

Argentic βγ-Dibrom-δ-Sulphopyromucate, $Ag_2C_5Br_2SO_6.H_2O$.—
The silver salt is sparingly soluble in cold water, more readily in hot, and crystallises in large rhombic plates.

1.0216 gram of the air-dried salt lost, at 120°, 0.0339 gram H_2O.

	Calculated for $Ag_2C_5Br_2SO_6.H_2O$.	Found.
H_2O	3.09	3.31

I. 0.3016 gram of the salt dried at 120° gave 0.1520 gram AgCl.
II. 0.3021 gram of the salt dried at 120° gave 0.1522 gram AgCl.

	Calculated for $Ag_2C_5Br_2SO_6$.	Found. I.	II.
Ag	38.30	37.93	37.93

Potassic βγ-Dibrom-δ-Sulphopyromucate, $K_2C_5Br_2SO_6.H_2O$.—
The potassium salt is readily soluble in hot water, more sparingly soluble in cold water. It crystallises in flat, obliquely truncated prisms.

I. 1.0634 gram of the air-dried salt lost, at 135°, 0.0377 gram H_2O.

II. 0.5307 gram of the air-dried salt gave 0.2072 gram K_2SO_4.

	Calculated for $K_2C_5Br_2SO_6.H_2O$.	Found. I.	II.
H_2O	4.05	3.55	...
K	17.60	...	17.53

0.4507 gram of the salt dried at 135° gave 0.1823 gram K_2SO_4.

	Calculated for $K_2C_5Br_2SO_6$.	Found.
K	18.35	18.16

From the structure of the βγ-dibrompyromucic acid, which has already been determined by Hill and Sanger,[1] it is evident that a sulphonic acid formed from it must of necessity contain the sulpho group in the δ position. It therefore seemed to us of interest to prepare from this βγ-dibrom-δ-sulphopyromucic acid, by the elimination of the bromine, the corresponding sulphopyromucic acid. Should this acid prove to be identical with that made directly from pyromucic acid by means of sulphuric acid, the δ position of the sulpho group in the latter acid would be established with precision. A strongly ammoniacal solution of baric βγ-dibrom-δ-sulphopyromucate was warmed for some time with an excess of zinc dust. After reduction had taken place the filtered solution was boiled with an excess of baric hydrate until the ammonia had been expelled, and the excess of baric hydrate then removed with carbonic dioxide. The concentrated solution deposited on cooling hemispherical aggregations of colorless crystals, which upon investigation proved to be identical in composition with the baric sulphopyromucate already described, and to have also the same solubility in cold water.

0.6194 gram of the air-dried salt lost, at 160°, 0.1111 gram H_2O, and gave 0.3614 gram $BaSO_4$.

[1] Proceedings Amer. Acad. **21**, 181.

	Calculated for $BaC_5H_2SO_6.4H_2O$.	Found.
H_2O	18 02	17.94
Ba	34.34	34.30

I. 12.9988 grams of the solution saturated at 21° gave 0.3169 gram $BaSO_4$.

II. 13.0993 grams of the solution saturated at 21° gave 0.3181 gram $BaSO_4$.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt :

I.	II.
3.42	3.41

It will be seen that these results prove the identity of this salt with that made directly from pyromucic acid.

Action of Bromine.

Bromine in aqueous solution readily oxidises $\beta\gamma$-dibrom-δ-sulphopyromucic acid or its salts. If a slight excess of bromine is added to an aqueous solution of the barium salt, baric sulphate is at once precipitated, and after the reaction is completed by gentle heat, ether extracts from the filtered solution dibrommaleic acid. The anhydride formed by sublimation was found to melt at the proper point, 114°–115°.

Action of Nitric Acid.

Diluted nitric acid oxidises $\beta\gamma$-dibrom-δ-sulphopyromucic acid on heating and forms dibrommaleic acid, whose identity we established through the melting point of its anhydride, 114°–115°. By the action of fuming nitric acid a nitro acid is formed. The dry acid was slowly added to several times its weight of fuming nitric acid. At first the mixture was cooled, afterwards warmed, and the greater part of the nitric acid then expelled by gentle heat. The crystalline product of the reaction was in part an acid quite readily soluble in hot water, and in part a neutral substance which dissolved with more difficulty in boiling water. For the complete separation of these two substances we treated the product with a dilute solution of sodic carbonate and extracted with ether. The alkaline solution was then acidified and the acid extracted with ether. After several recrystallisations from hot water it formed finely felted yellow needles, which were sparingly soluble in cold water, more readily in hot, and melted at 204°–205°. They dissolved freely in

alcohol, ether, or in benzol.   Analysis showed the substance to be
a dibromnitropyromucic acid.

I. 0.1050 gram of the acid gave 0.1260 gram AgBr.

II. 0.2970 gram of the acid gave 11.7 cc. of moist nitrogen at 21°
under a pressure of 758 mm.

	Calculated for $C_5HBr_2(NO_2)O_3$.	Found.
Br	50.79	51.07
N	4.44	4.47

The mode of its formation shows that this acid must of necessity
be the $\beta\gamma$-dibrom-δ-nitropyromucic acid.

The ether which had been used for extracting the alkaline solu-
tion of the crude nitro product left, on evaporation, a quantity of a
yellow crystalline solid which was sufficient to enable us to estab-
lish its identity by analysis.   The substance was sparingly soluble
even in hot water, and crystallised on slow cooling in stout prisms,
or on rapid cooling and scratching in felted needles.   In alcohol
it was sparingly soluble ; but benzol dissolved it freely, and on
standing the solution deposited quite large transparent yellow
prisms which effloresced rapidly on exposure to the air.   The
melting point to the effloresced substance was 150°–151°, and the
percentage of bromine it contained showed that it was a dibromdi-
nitrofurfuran.

0.2008 gram of the substance gave 0.2396 gram AgBr.

	Calculated for $C_4Br_2(NO_2)_2O$.	Found.
Br	50.63	50.79

The clear crystals deposited from benzol evidently contained
benzol of crystallisation.   They effloresced so rapidly, however,
that the exact determination of the combined benzol was somewhat
difficult.

0.2611 gram of the substance rapidly pressed and weighed lost,
on standing exposed to the air until the weight was constant, 0.0486
gram benzol.

	Calculated for $C_4Br_2(NO_2)_2O.C_6H_6$.	Found.
C_6H_6	19.80	18.61

Considering the difficulty of such determinations, this result
leaves no doubt that this dibromdinitrofurfuran crystallises with
one molecule of benzol.   The mode of formation of this substance
leaves no possible doubt that it is the $\alpha\alpha$-dinitro-$\beta\beta$-dibromfurfuran.

(*To be concluded.*)

ON THE DENSITIES AND REFRACTIVE INDICES OF CERTAIN OILS.

By J. H. Long.

In the course of a somewhat extended investigation on fats and oils I found it desirable to make full determinations of specific gravity and index of refraction.

For some oils these data are not to be found in the literature, and in most cases where given they are more or less incomplete. In the following pages I present the results obtained with oils of known purity, and will describe first the method of experiment.

Specific Gravity.

This was found by means of a 50 gram pycnometer with capillary stopper, and was determined at four temperatures obtained by immersion in water in the usual manner. A large volume of water was employed and its temperature kept constant, as shown by an accurately corrected thermometer. The temperature of the oil in the vessel was known to a tenth of one degree C. The volume and cubic expansion of the pycnometer were determined by special experiments. In the final reductions all weights were calculated to the value in vacuo, and the specific gravities referred to water at 4° C. as unity.

The Index of Refraction.

For these determinations I employed the method of minimum deviation, making use of an excellent Meyerstein spectrometer and hollow prism from which readings to 30″ could be obtained. The refractive index is given by the formula $N = \dfrac{\sin\dfrac{A+d}{2}}{\sin\dfrac{A}{2}}$ in which A is the refractive angle of the prism and d the observed angle of minimum deviation. Some of the experiments were carried out in a cold room in winter, while others were performed in the summer. To determine the refraction at higher temperatures, the prism, resting on its brass table, was placed on a warm iron plate, and allowed to remain there until a thermometer inserted in the top opening of the prism showed the required

elevation. The prism and table were then returned to the instrument, their position was adjusted by means of leveling screws and the readings commenced. (The arrangement of the apparatus is shown in Wüllner's Lehrbuch der experimental Physik, II, 129). By making duplicate experiments, and taking the mean values, results accurate to four decimal places of N are obtained. In the following tables the corrected temperature readings are given, the thermometer used being the same as that employed in the determination of density. As source of light I used the sodium flame obtained by fusing a bead of sodium carbonate over a Bunsen burner.

Olive Oil.

We find various statements in the books regarding the density of pure olive oil. For a temperature of 15° C. the values vary from .9120 to .9250, or even higher. Many chemists claim that these limits are too wide for pure oils, but it must be remembered that the products are extracted and refined by quite different processes. The hot pressed oils contain considerable palmitin, solidify, therefore, sooner, and show a higher density. Out of a number of samples examined I can report on four of known purity. One of these samples was pressed in Southern California from native olives; the others were pressed in France. Not one of these samples deposited palmitin above 0° C. Although thick, they remained perfectly clear, which suggests to me that the statements usually found in the books regarding the temperature of solidification of olive oil must have been derived from a study of inferior or warm pressed oils rich in palmitin. Allen, however, gives the solidifying point as $+ 4$ to $- 6°$ C.

The specific gravity (D) and the refractive index (N) of these oils I found as follows:

No. 1. Pressed in France.

T.	D.	T.	N.
3.5°	.9240	14.5°	1.4716
19.5	.9131	20.5	1.4693
36.0	.9022	23.5	1.4681
45.9	.8955	26.6	1.4673
		30.7	1.4657
		35.9	1.4637
		41.1	1.4620

No. 5. Pressed in California.

T.	D.	T.	N.
4.5°	.9240	16.3°	1.4712
18.0	.9149	19.3	1.4700
31.1	.9062	23.4	1.4684
49.7	.8938	25.4	1.4677
		29.3	1.4663
		34.3	1.4643
		39.3	1.4622

No. 10. Pressed in France.

T.	D.	T.	N.
2.6°	.9252	15.8°	1.4731
19.5	.9132	20.3	1.4708
33.5	.9039	23.3	1.4694
49.4	.8935	24.8	1.4687
		26.8	1.4679
		30.8	1.4663
		42.2	1.4626

No. 11. Pressed in France.

T.	D.	T.	N.
4.4°	.9238	14.8°	1.4734
19.8	.9128	17.3	1.4722
32.5	.9044	19.3	1.4714
50.6	.8924	21.8	1.4703
		24.3	1.4693
		27.8	1.4677
		30.8	1.4665
		34.3	1.4651

The variation in the specific gravity seems to be the same for all samples, and amounts to about .00066 for each degree. Schaedler (Technologie der Fette und Oele u. s. w.) gives almost the same coefficient for pure samples, and .9177 as the specific gravity at 15° C. Allen gives .914 to .917 as the probable variations. Quincke (Ber. Acad. Ber. 1883, 409) gives 1.4690 as the value of the refractive index at 20.5° C.

This is close to the values found for Nos. 1 and 5, but somewhat lower than those found for Nos. 10 and 11.

The temperature variation of N amounts to nearly .0004 for each degree between 20° and 35°.

Cottonseed Oil.

Because of the great practical importance and increasing consumption of this article, I have made numerous tests of samples obtained from different sources. In the last few years great improvements have been made in the processes of refining cottonseed oil, in consequence of which much of the product now on the market does not correspond to the tests usually given. Cottonseed oil can be refined (and practically is) until it is as clear and light as water. Such an oil contains few of the coloring or readily oxidisable matters which give the so-called *color* or *heat* reactions so often employed. The cold test (solidifying point) of such oils is likewise very much altered, and their detection when mixed with other oils made more difficult.

I have obtained the following results by direct experiment.

No. 7. A crude oil obtained in Chicago from a leading refiner. It deposits a sediment quickly when cooled below 15° C.

T.	D.	T.	N.
3.0°	.9325	27.9°	1.4694
16.6	.9233	35.3	1.4668
32.4	.9126	46.2	1.4624
46.5	.9030		

The specific gravity determination at the lowest temperature is probably somewhat inaccurate.

No. 8. A light yellow oil refined from No. 7. Remains clear at lowest temperature.

T.	D.	T.	N.
4.5°	.9291	19.3°	1.4744
18.2	.9198	22.8	1.4730
30.9	.9112	24.8	1.4722
45.4	.9014	28.3	1.4708
		36.3	1.4675
		44.2	1.4658

No. 9. A sample refined from No. 8. This is white and clear and bears no resemblance to ordinary cottonseed oils.

T.	D.	T.	N.
2.0°	.9312	18.3°	1.4736
17.9	.9202	22.3	1.4720
34.3	.9090	27.3	1.4700
47.0	.9006	31.3	1.4684
		35.3	1.4669
		40.2	1.4650

No. 12. A crude oil, very dark, but deposits a comparatively small sediment on cooling to 15° C. and below.

The sample is too dark for accurate determinations of the refractive index.

T.	D.	T.	N.
4.8°	.9290	21.0°	1.4708
18.6	.9199	23.0	1.4700
32.5	.9107		
49.6	.8994		

No. 6. A sample refined from the above in the laboratory, by partial saponification with a 1 per cent. solution of sodium carbonate, washing, and drying by means of a current of hot air. The product is yellow but perfectly clear.

T.	D.	T.	N.
3.8°	.9295	13.8°	1.4755
19.2	.9191	19.3	1.4730
31.4	.9108	23.3	1.4712
47.4	.9000	26.3	1.4703
		32.3	1.4681
		36.2	1.4667
		39.2	1.4660

No. 16. A clear yellow sample refined in New York.

T.	D.	T.	N.
0.7°	.9322	19.3°	1.4742
15 6	.9219	22.8	1.4728
30.5	.9117	25.3	1.4718
46.5	.9013	27.8	1.4708
		29.8	1.4700
		33.3	1.4686
		36.8	1.4672

The figures given above show that the temperature variations of specific gravity and refractive index are not very different from those of olive oil. The decrease in specific gravity at mean temperatures varies in the different samples between .00066 and .00068, while the variations in the refractive index are something less than .0004 for each degree.

The values found for the specific gravity of the crude samples are lower than those usually given, as will appear below.

Sesamé Oil.

Although this oil is made in large quantities in Europe, it is difficult to secure specimens here of guaranteed purity.

No. 4. A sample received from a Chicago importer.

T.	D.	T.	N.
3.3°	.9308	17.9°	1.4744
16.5	.9218	20.4	1.4733
32.4	.9111	24.4	1.4718
48.8	.9001	29.4	1.4698
		32.4	1.4687
		36.4	1.4672
		39.3	1.4661

No. 14. A sample refined from the above by treatment with a 1 per cent. solution of potassium hydrate.

T.	D.	T.	N.
1.5°	.9326	14.3°	1.4771
18.5	.9209	18.3	1.4755
33.2	.9110	22.8	1.4736
47.4	.9016	24.8	1.4728
		26.8	1.4720
		30.3	1.4705
		34.3	1.4691
		39.2	1.4673

No. 18. A sample received from a New York importer.

T.	D.	T.	N.
5.5°	.9282	14.3°	1.4759
18.4	.9192	19.3	1.4739
34.6	.9081	20.3	1.4736
46.6	.8998	23.3	1.4724
		26.8	1.4710
		30.3	1.4694
		34.3	1.4678
		38.0	1.4664

The temperature changes are nearly identical with those given for olive and cottonseed oil, varying for the density between .00067 and .00069 for each degree.

Mustard Oil.

The oil of black mustard may be classed among the cheaper oils, and when properly refined has numerous uses. I have

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examined two samples of known purity, and a third prepared from one of these by partial saponification. The first two had been well refined and were almost entirely free from the odor of the volatile oil.

No. 2.　A sample obtained in Chicago.

T.	D.	T.	N.
4.0°	.9222	14.5°	1.4769
19.1	.9122	17.5	1.4751
34.0	.9026	20.5	1.4739
48.6	.8932	22.5	1.4732
		24.5	1.4724
		28.9	1.4706
		35.0	1.4683
		40.0	1.4663

No. 15.　Oil refined from the above by treatment with a 1 per cent. solution of potassium hydrate.

T.	D.	T.	N.
1.5°	.9251	14.8°	1.4771
16.6	.9149	19.3	1.4749
33.6	.9037	21.3	1.4739
47.4	.8946	23.3	1.4729
		25.8	1.4720
		31.3	1.4700
		34.3	1.4688
		37.3	1.4677

No. 17.　A sample obtained from a New York importer.

T.	D.	T.	N.
1.7°	.9239	15.3°	1.4759
18.6	.9128	19.3	1 4743
36.0	.9014	21.3	1.4736
45.8	.8948	23.8	1.4726
		27.3	1.4712
		31.8	1.4694
		36.8	1.4674
		39.3	1.4665

The temperature coefficients are nearly as observed in the other oils.

Peanut Oil.

One sample of oil, partially refined, was examined, with these results.

No. 19.

T.	D.		T.	N.
$3.2°$	.9309		$15.8°$	1.4736
17.9	.9186		19.8	1.4718
34.4	.9074		23.3	1.4704
47.7	.8984		25.3	1.4696
			28.3	1.4684
			34.3	1.4661
			39.2	1.4641

While the change in the density is comparatively rapid between the lowest temperatures, it amounts to .00068 for each degree between the mean temperatures, that is, the rate is about as before given. The variation in the refractive index is normal.

Castor Oil.

The following results were obtained by examination of a sample of well refined cold pressed oil.

No. 3.

T.	D.		T.	N.
$4.0°$	.9695		$14.4°$	1.4831
7.1	.9675		18.4	1.4806
18.0	.9602		20.4	1.4790
32.5	.9505		22.9	1.4781
46.8	.9410		25.4	1.4771
			28.4	1.4759
			33.9	1.4741
			37.3	1.4728

Lard Oil.

A sample of pure oil, pressed in Chicago, was examined and gave these figures. As it became thick at the lowest temperature, the density determination at that point is probably not quite accurate.

No. 13.

T.	D.		T.	N.
$1.8°$	.9287		$20.3°$	1.4685
15.5	.9154		24.3	1.4669
32.5	.9036		27.3	1.4657
48.5	.8926		29.3	1.4649
			32.3	1.4637
			36.3	1.4622
			39.2	1.4612

In order to compare the values for the different oils with each other as well as with similar data obtained by other observers, I have calculated from the above direct observations the numbers in the tables below. In most cases the curve representing the variations in specific gravity is nearly a straight line, and without introducing appreciable error it can be taken as linear between the intermediate temperatures. Assuming these points as correctly determined, I have interpolated values from 18° to 25° and for 30° and 35°.

By means of carefully drawn curves I have interpolated, from the direct determinations of N, the values for the same degrees of temperature. The numbers thus obtained are undoubtedly as accurate and satisfactory as could be obtained by a laborious method of calculation. Finally, I have calculated the "specific refractive energy," $\frac{N-1}{D}$, and give these values in another column.

	Olive Oil, 1.				*Olive Oil*, 11.		
T.	D.	N.	$\frac{N-1}{D}$.	T.	D.	N.	$\frac{N-1}{D}$.
18	.9141	1.4702	.5144	18	.9139	1.4719	.5164
19	.9134	1.4698	.5143	19	.9133	1.4715	.5163
20	.9127	1.4695	.5143	20	.9126	1.4711	.5162
21	.9121	1.4691	.5143	21	.9119	1.4707	.5162
22	.9114	1.4688	.5144	22	.9112	1.4703	.5161
23	.9107	1.4684	.5143	23	.9106	1.4698	.5159
24	.9101	1.4680	.5142	24	.9099	1.4694	.5159
25	.9094	1.4677	.5143	25	.9093	1.4690	.5158
30	.9061	1.4658	.5142	30	.9060	1.4669	.5153
35	.9028	1.4640	.5140	35	.9027	1.4648	.5148

	Olive Oil, 10.				*Olive Oil*, 5.		
T.	D.	N.	$\frac{N-1}{D}$.	T.	D.	N.	$\frac{N-1}{D}$.
18	.9142	1.4718	.5161	18	.9149	1.4704	.5142
19	.9135	1.4714	.5160	19	.9142	1.4701	.5142
20	.9129	1.4709	.5158	20	.9136	1.4697	.5141
21	.9122	1.4705	.5158	21	.9129	1.4693	.5141
22	.9115	1.4701	.5157	22	.9122	1.4690	.5141
23	.9109	1.4696	.5155	23	.9116	1.4685	.5140
24	.9102	1.4692	.5155	24	.9109	1.4682	.5140
25	.9095	1.4688	.5154	25	.9103	1.4678	.5139
30	.9062	1.4666	.5149	30	.9069	1.4659	.5137
35	.9029	1.4645	.5148	35	.9036	1.4640	.5135

Cottonseed Oil, 6.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9199	1.4735	.5147
19	.9192	1.4731	.5147
20	.9186	1.4727	.5146
21	.9179	1.4724	.5147
22	.9172	1.4720	.5147
23	.9165	1.4716	.5146
24	.9158	1.4712	.5145
25	.9151	1.4709	.5147
30	.9118	1.4690	.5144
35	.9084	1.4671	.5142

Cottonseed Oil, 8.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9199	1.4749	.5163
19	.9193	1.4745	.5162
20	.9186	1.4741	.5161
21	.9179	1.4737	.5161
22	.9172	1.4733	.5160
23	.9165	1.4729	.5160
24	.9159	1.4725	.5159
25	.9151	1.4721	.5159
30	.9118	1.4700	.5155
35	.9084	1.4680	.5152

Cottonseed Oil, 7.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9224	1.4729	.5127
19	.9217	1.4725	.5127
20	.9210	1.4722	.5127
21	.9203	1.4718	.5127
22	.9196	1.4715	.5127
23	.9190	1.4711	.5126
24	.9183	1.4708	.5127
25	.9176	1.4704	.5127
30	.9142	1.4687	.5127
35	.9109	1.4670	.5127

Cottonseed Oil, 9.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9201	1.4737	.5148
19	.9194	1.4733	.5148
20	.9188	1.4730	.5148
21	.9180	1.4726	.5148
22	.9174	1.4722	.5147
23	.9167	1.4718	.5147
24	.9160	1.4714	.5146
25	.9154	1.4710	.5145
30	.9119	1.4690	.5143
35	.9085	1.4671	.5141

Cottonseed Oil, 12.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9203		
19	.9196		
20	.9190		
21	.9183	1.4708	.5127
22	.9176		
23	.9170	1.4700	.5125
24	.9163		
25	.9157		
30	.9124		
35	.9090		

Sesamé Oil, 4.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9208	1.4742	.5150
19	.9201	1.4738	.5149
20	.9194	1.4735	.5150
21	.9188	1.4731	.5149
22	.9181	1.4727	.5149
23	.9174	1.4723	.5148
24	.9167	1.4719	.5148
25	.9161	1.4715	.5147
30	.9127	1.4696	.5145
35	.9093	1.4677	.5144

Cottonseed Oil, 16.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9203	1.4747	.5158
19	.9196	1.4743	.5158
20	.9189	1.4739	.5157
21	.9182	1.4735	.5157
22	.9176	1.4731	.5156
23	.9168	1.4727	.5156
24	.9162	1.4723	.5155
25	.9155	1.4719	.5155
30	.9120	1.4699	.5153
35	.9086	1.4679	.5150

Sesamé Oil, 14.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9212	1.4756	.5163
19	.9206	1.4752	.5162
20	.9199	1.4748	.5161
21	.9192	1.4744	.5161
22	.9185	1.4740	.5161
23	.9179	1.4736	.5160
24	.9172	1.4732	.5159
25	.9165	1.4728	.5159
30	.9132	1.4708	.5156
35	.9098	1.4688	.5153

Sesamé Oil, 18.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9195	1.4744	.5159
19	.9188	1.4740	.5159
20	.9181	1'4736	.5158
21	.9174	1.4732	.5158
22	.9167	1.4728	.5158
23	.9160	1.4724	.5157
24	.9154	1.4720	.5157
25	.9147	1.4716	.5156
30	.9113	1.4695	.5152
35	.9078	1.4675	.5150

Mustard Oil, 15.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9140	1.4754	.5201
19	.9133	1.4750	.5201
20	.9127	1.4746	.5200
21	.9120	1.4742	.5200
22	.9113	1.4738	.5199
23	.9107	1.4733	.5197
24	.9100	1.4730	.5198
25	.9094	1.4726	.5197
30	.9060	1.4705	.5193
35	.9028	1.4685	.5189

Mustard Oil, 2.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9129	1.4749	.5203
19	.9123	1.4745	.5201
20	.9116	1.4741	.5201
21	.9109	1.4737	.5199
22	.9103	1.4733	.5199
23	.9097	1.4729	.5198
24	.9090	1.4725	.5198
25	.9084	1.4722	.5198
30	.9052	1.4702	.5194
35	.9020	1.4683	.5192

Mustard Oil, 17.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9132	1.4748	.5199
19	.9125	1.4744	.5199
20	.9119	1.4740	.5198
21	.9112	1.4736	.5198
22	.9106	1.4732	.5197
23	.9099	1.4728	.5196
24	.9093	1.4724	.5195
25	.9086	1.4721	.5196
30	.9053	1.4701	.5193
35	.9021	1.4681	.5189

	Castor Oil, 3.				Lard Oil, 13.		
T.	D.	N.	$\frac{N-1}{D}$.	T.	D.	N.	$\frac{N-1}{D}$.
18	.9602	1.4799	.4998	18	.9137	1.4694	.5137
19	.9595	1.4795	.4997	19	.9130	1.4690	.5137
20	.9589	1.4791	.4996	20	.9122	1.4686	.5137
21	.9582	1.4788	.4997	21	.9116	1.4682	.5136
22	.9575	1.4784	.4996	22	.9109	1.4678	.5136
23	.9569	1.4780	.4995	23	.9102	1.4674	.5135
24	.9562	1.4777	.4996	24	.9095	1.4670	.5135
25	.9555	1.4773	.4995	25	.9088	1.4666	.5134
30	.9522	1.4755	.4994	30	.9053	1.4647	.5133
35	.9488	1.4738	.4994	35	.9019	1.4627	.5130

Peanut Oil, 19.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9187	1.4725	.5143
19	.9180	1.4721	.5143
20	.9173	1.4717	.5142
21	.9164	1.4713	.5143
22	.9157	1.4709	.5143
23	.9151	1.4705	.5142
24	.9144	1.4701	.5141
25	.9138	1.4696	.5139
30	.9103	1.4678	.5139
35	.9069	1.4658	.5136

The numbers in the column headed $\frac{N-1}{D}$ are not quite constant, but do not vary more than is the case with many organic substances. In most cases the refractive index seems to decrease somewhat more rapidly than does the specific gravity.

The saponification equivalents found for several of these oils, sesamé, olive, and cottonseed, show a mean molecular weight of about 870. From this the *molecular* refractive energy, $M\left(\frac{N-1}{D}\right)$, is about 448, which coincides very well with the atomic refractive energies, $C = 4.85$, $H = 1.50$, and $O = 3$.

If an oil in the above table contained only tri-olein these numbers would lead to 450.4. A mixture of tri-olein and tri-stearin would yield nearly the same result; while tri-palmitin, having a lower

molecular weight, would make the number slightly smaller. A mixture of 8 parts of tri-olein and 2 parts of tri-palmitin would give 447.2, and this is approximately the composition of the above oils.

In the olive oils the specific gravity at 20° C. varies between .9126 and .9136. These values are about the same as commonly given for the finest cold pressed oils and are within the limits of the United States and British Pharmacopœias. Schaedler gives .9143 as the specific gravity of a pure sample at 20°, but states that in hot pressed oils rich in palmitin it may be as high as .922 at the same temperature. The refractive indices at 20° vary from 1.4695 to 1.4711, and the specific refractive energy from .5143 to .5162 at the same temperature.

In the six samples of cottonseed oil examined the variations in the specific gravity at 20° are between .9186 and .9210. These numbers are all greater than those with olive oil. The refractive indices vary from 1.4722 to 1.4741, and the refractive energies between .5127 and .5161 at 20°. These last numbers are nearly the same as with olive oil.

It will be noticed that the values given for the specific gravity are much lower than those usually quoted. Allen places the density of the crude oil between .928 and .930, with that of the refined between .922 and .926. Dietrich (Dingler's Poly. Jour. 1885, 127) places the density of the pure oil at 23° between .917 and .921. These numbers have evidently been obtained from samples richer in palmitin than were those examined by me.

In the three samples of sesamé oil the specific gravity at 20° varies between .9181 and .9199, the refractive indices between 1.4735 and 1.4748, and the quotient $\frac{N-1}{D}$ between .5150 and .5161. These numbers are similar to those for cottonseed oil.

In mustard oil the density is lower; at 20° the three samples vary between .9116 and .9127, their refractive indices between .14740 and 1.4746, and the refractive energies between .5198 and .5201. These figures are higher than found for other oils and may have a practical value. In castor oil we have a high gravity and low refractive energy.

The specific gravities found for lard oil and peanut oil do not differ materially from those usually given, and there seems to be nothing unusual about the refraction.

In many cases determinations of refractive index have a practical use in the identification of organic liquids and also in quantitative valuation.

Alex. Müller has recently proposed the use of the Abbé refractometer in the examination of butter, and Skalweit (Rept. anal. Chem. 1886, pp. 181 and 235) has carried out a number of tests to show the value of the method. It appears from his tests that *butter oleine* (separated after melting by partial cooling and pressure) has a lower refractive index than any oil in the above table, and also lower than that of the various solid products as butterine and oleomargarine.

Skalweit's observations have undoubtedly a practical value, but his method necessitates the use of the Abbé refractometer. I have found that results almost as sharp can be obtained by using solutions of the fats made with definite mixtures of alcohol and chloroform, and determining the minimum deviation in the usual manner with the Meyerstein or similar instrument. The above experiments show that a determination of the refractive power coupled with that of the specific gravity may prove of value in the identification of other fatty oils.

CHICAGO, *December*, 1887.

ON THE TREATMENT OF NATURAL SILICATES WITH HYDROCHLORIC ACID AS A MEANS OF ASCERTAINING THEIR STRUCTURE.

BY E. A. SCHNEIDER.

In the March number of this journal, Professor F. W. Clarke has published some very interesting remarks on the chemical structure of natural silicates. In speaking of the real difficulties which are met with in this kind of researches, Professor Clarke observes very justly that though it is not possible to ascertain the true molecular weight of silicates on account of their being non-volatile solids, their chemical structure can be determined by the study, for instance, of the alterations they undergo in nature. Now, it is a well known fact that alterations through weathering are

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chiefly due to the carbonic acid of the air. The action of carbonic acid on minerals has been undoubtedly tried in chemical laboratories, but no decisive results are recorded. This may be partially due to the fact that this process is too slow for the patience of the average chemist. In this respect hydrochloric acid is preferable. It acts more quickly and with more energy on the natural silicates than carbonic acid; some silicates are completely decomposed by it, some partially, and some not attacked at all. This varying behavior of the silicates towards hydrochloric acid has been made use of by the authors of mineralogical tables for the purposes of classification, but to derive from these facts new material for the explanation of the structure of the natural silicates has apparently not been thought of. And still it seems to be promising.

Supposing a number of silicates which contain the same constituents, but in varying proportions, whose relationship has been made probable by many indications, and which are partially decomposed by hydrochloric acid, should be treated under exactly the same conditions with hydrochloric acid, and it should be found that various but gradually increasing or decreasing amounts of the same constituents have been extracted, should we not to some extent be entitled to arrange the members of such a series of silicates accordingly and draw some conclusions as to their structure?

The contemplation of the structural formulas which Professor Clarke gives for grossularite, prehnite and anorthite, in conjunction with the behavior of these silicates towards hydrochloric acid, may help to illustrate this view.

$$
\text{Al} \underset{\diagdown \text{SiO}_4 \equiv \text{Al}}{\overset{\diagup \text{SiO}_4 \equiv}{-\text{SiO}_4 \equiv}} \Big\} \text{Ca}_3
\qquad
\text{Al} \underset{\diagdown \text{SiO}_4 \equiv \text{Al}}{\overset{\diagup \text{SiO}_4 \equiv \text{CaH}}{-\text{SiO}_4 \equiv \text{CaH}}}
\qquad
\text{Al} \underset{\diagdown \text{SiO}_4 \equiv \text{Al}}{\overset{\diagup \text{SiO}_4 \equiv \text{CaH}}{-\text{SiO}_4 \equiv \text{Al}}}
$$

Grossularite.   Prehnite.   Anorthite.
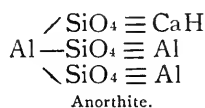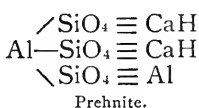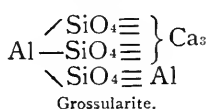
We observe in this series of formulas a remarkable gradation; and we observe the same gradation in the behavior of these silicates towards hydrochloric acid: grossuralite is insoluble in hydrochloric acid, prehnite is decomposed by this acid without gelatinising, and a certain variety of anorthite (from Mount Somma, according to Dana) with separation of gelatinous silica.

The fact that grossularite gelatinises with hydrochloric acid after ignition is also of some interest. It is possible that ignition modifies the structure of the grossularite in a way which approaches it very near to prehnite and anorthite.

The hypothesis of Sterry Hunt and of Tschermak, that the triclinic feldspars consist of various mixtures between albite and anorthite as two extremes, appears to be confirmed also by the behavior of the triclinic feldspars towards hydrochloric acid. Anorthite is soluble and albite insoluble in hydrochloric acid. Oligoclase, which is mainly a soda feldspar with a small percentage of lime, is "not materially acted upon by acids" (Dana); andesite, which contains more lime, is said to be "imperfectly soluble in acids" (Dana); and labradorite, which is the richest in lime of all the triclinic feldspars, is, according to B. v. Cotta,[1] "unlike other feldspars, thoroughly soluble in heated muriatic acid." According to Dana, it "is decomposed with difficulty by muriatic acid, generally leaving a portion of undecomposed mineral."

Do the hydrochloric acid extracts contain mainly lime salts, or sodium and lime salts proportionately to the lime and soda in the feldspars? These questions are certainly worthy of consideration, and if answered, would throw some additional light on the theory of Sterry Hunt and Tschermak.

Next to the triclinic feldspars, the minerals of the amphibole group show a peculiar behavior towards hydrochloric acid. B. v. Cotta[2] makes the statement that the "varieties of amphibole richest in iron are partially decomposed by muriatic acid; other varieties are little affected by that acid." If we class wollastonite, $CaSiO_3$, in this group, we have, however, a notable exception. This silicate gelatinises readily with hydrochloric acid. This fact is peculiarly interesting, as another metasilicate which belongs to this group, enstatite, $MgSiO_3$, is perfectly insoluble in hydrochloric acid. Moreover, wollastonite and enstatite show differences in their crystallographic character; the first is monoclinic, the second orthorhombic.

As the magnesia-lime silicates of the amphibole group can be considered, at least chemically, as wollastonite or as enstatite in which a part of the lime has been substituted by magnesia and *vice versa*, and some of these minerals are partially decomposed by hydrochloric acid, a similar line of research as in the case of the triclinic feldspars is indicated.

It is known of some minerals of the amphibole group (as well as of those of the garnet group) which contain ferrous oxide, that their decomposition by muriatic acid is very superficial, and

[1] "Rocks Classified and Described." B. v. Cotta.   [2] Ibid.

that they yield to the acid nothing but iron. This interesting peculiarity has not been further studied, although the amphibole group contains material enough for such an investigation if we take into consideration the great range of variations in the percentages of ferrous oxide among the minerals of this group. The fact that in many instances the ferrous oxide is found together with one only of the oxides of calcium or magnesium should facilitate a comparative investigation.

I give here, to illustrate this view, a number of analyses from J. D. Dana's "System of Mineralogy."

	Antholithe, magnesia-iron amphibole.[1]	Hypersthene.[2]	Hedenbergite, iron-lime pyroxene.[3]	Cummingtonite, iron-magnesia amphibole.[4]	Hypersthene.[5]	Grisnerite, iron amphibole.[6]
SiO_2	55.20	52.88	47.78	51.09	51.35	43.9
Al_2O_3	...	3.90	...	.95	...	1.9
FeO	11.82	18.23	27.01	32.07	33.92	52.2
MnO	...	...	...	1.50	...	...
MgO	30.37	22.22	...	10.29	11.09	...
CaO	...	3.55	22.95	tr.	1.84	.5
H_2O	2.25	.56	...	3.04	.50	...
Na_2O	...	...	...	.75	...	...

Some preliminary experiments have convinced me that the most trustworthy and uniform results will be obtained by digesting the finely triturated mineral powders with hydrochloric acid (which boils unchanged at 110° under the normal pressure) in sealed tubes[7] of hard glass. The most suitable (because the easiest to regulate) temperature for the digestions is that of boiling water at 760 mm. pressure. As I have at present no laboratory accommodations at my disposal, I should be happy to see if any of my fellow-workers deem it worth while to carry out experimentally some of my suggestions.

[1] From Staten Island, analysed by Beck. [2] From Harzburg, analysed by Streng.
[3] From Arendal, analysed by Wolff. [4] From Cummington, analysed by Smith and Brush.
[5] From Skye, analysed by Muir. [6] From Collobrières, analysed by Grisner.

[7] If the mineral powders are digested with the acid in open vessels, an unavoidable loss by evaporation takes place. As for the purposes of a comparative research it is important that all the experiments should be performed under strictly the same conditions, it would be necessary to replace the evaporated acid. I have found that by working in this manner, the greatest possible accuracy cannot be obtained, and propose therefore to use sealed tubes or other closed vessels.

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LXI.—ON SUBSTITUTED PYROMUCIC ACIDS.

SECOND PAPER.

BY HENRY B. HILL AND ARTHUR W. PALMER.

β-SULPHO-δ-BROMPYROMUCIC ACID.

The three sulphonic acids thus far described contain the sulpho-group in the δ position, and, in the two cases where the formation of isomeric products is theoretically possible, we have hitherto been unable to prove that any isomeric sulphonic acids are in reality formed. For the preparation of such isomeric products it was, therefore, evidently necessary to start with the δ-hydrogen atom otherwise replaced, and the δ-brompyromucic acid formed the most convenient material. We found no difficulty in preparing in this way a sulphonic acid which we have called the β-sulpho-δ-brompyromucic acid and from it the β-sulphopyromucic acid itself may be made. Since the brominated acid was of necessity first prepared, and we were able to investigate it more fully, it may be more conveniently first described.

δ-Brompyromucic acid dissolves in fuming sulphuric acid without essential decomposition, and after the lapse of some time the formation of the sulphonic acid appears to be complete. On neutralising the diluted solution with baric carbonate, a barium

salt is obtained which is sparingly soluble even in hot water, and which usually persistently retains a slight yellow or greenish color. The purification of this neutral salt is still further rendered difficult by the fact that a hot saturated solution of the salt deposits little or nothing on cooling, and recrystallisation therefore involves the evaporation of comparatively large quantities of liquid. The purification may be more conveniently effected by conversion into the more soluble acid salt, or by preparing the acid salt at the outset. The acid salt may easily be made by dissolving the neutral salt in hydrochloric acid somewhat diluted with water, and removing by recrystallisation the baric chloride formed. From a solution of the acid salt the neutral salt may again be precipitated by the addition of baric acetate, or of course by the addition of ammonic hydrate and the necessary quantity of baric chloride. The free acid made from the barium salt by exact precipitation with sulphuric acid forms oblique flat prisms or plates which deliquesce in moist air.

Baric β-Sulpho-δ-brompyromucate, $BaC_5HBrSO_6.5H_2O$.—The barium salt is sparingly soluble in hot or cold water, and crystallises in clear six-sided, clustered prisms. Its aqueous solution is precipitated by the addition of alcohol. The salt contains five molecules of water, four of which it loses slowly on exposure to the air, or more rapidly when heated to 100°.

I. 2.1588 grams of the salt dried by short exposure to the air lost, at 162°, 0.3806 gram H_2O.

II. 1.1795 gram of the salt dried by short exposure to the air lost, at 170°, 0.2010 gram H_2O.

	Calculated for $BaC_5HBrSO_6.5H_2O$.	I.	Found. II.
H_2O	18.14	17.63	17.88

I. 1.8574 gram of the salt dried at 100° lost, at 162°, 0.0792 gram H_2O.

II. 0.7262 gram of the salt dried at 100° lost, at 160°, 0.0317 gram H_2O.

	Calculated for $BaC_5HBrSO_6.H_2O$.	I.	Found. II.
H_2O	4.25	4.28	4.37

I. 0.6945 gram of the salt dried at 160° gave 0.3980 gram $BaSO_4$.

II. 0.7840 gram of the salt dried at 140° gave 0.4500 gram $BaSO_4$.

III. 0.7825 gram of the salt dried at 140° gave 0.4495 gram BaSO₄.

	Calculated for BaC₅HBrSO₆.	I.	Found. II.	III.
Ba	33.75	33.69	33.75	33.77

We also determined the solubility of the salt in water at ordinary temperatures. Since the hot saturated solution deposited little or nothing on cooling, we prepared the solution by boiling down the hot aqueous solution until the salt began to separate. On cooling this supersaturated solution, abundant crystals were deposited.

I. 32.6032 grams of the solution saturated at 20° gave 0.5016 gram BaSO₄.

II. 33.7864 grams of the solution saturated at 20° gave 0.5194 gram BaSO₄.

The aqueous solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt:

I.	II.
2.68	2.68

Acid Baric β-Sulpho-δ-brompyromucate, Ba(C₅H₂BrSO₆)₂ 4H₂O.—This salt is most easily prepared by dissolving the neutral barium salt in diluted hydrochloric acid. It is readily soluble in hot water, sparingly in cold water, and crystallises in large well formed prisms which appear to be triclinic. The salt loses nothing when exposed to the air, or over sulphuric acid, and the loss at 100° is also insignificant. At 130° it slowly loses in weight, but turns brown and suffers partial decomposition before complete dehydration is reached.

I. 0.7884 gram of the air-dried salt gave 0.2456 gram BaSO₄.

II. 0.7804 gram of the air-dried salt gave 0.2460 gram BaSO₄.

	Calculated for Ba(C₅H₂BrSO₆)₂.4H₂O.	I.	Found. II.
Ba	18.29	18.32	18.53

Calcic β-Sulpho-δ-brompyromucate, CaC₅HBrSO₆.2H₂O.—The calcium salt is quite readily soluble in cold water, and its solubility is but little increased by heat. It crystallises in compactly aggregated oblique prisms, which are permanent in the air, and lose but little in weight over sulphuric acid or when heated to 100°.

I. 1.7804 gram of the air-dried salt lost, at 205°, 0.1767 gram H₂O.

II. 0.6483 gram of the air-dried salt gave 0.2544 gram CaSO₄.

	Calculated for $CaC_5HBrSO_6.2H_2O.$	Found. I.	Found. II.
H_2O	10.42	9.92	
Ca	11.60		11.54

I. 0.4645 gram of the salt dried at 200° gave 0.2015 gram $CaSO_4$.

II. 0.4026 gram of the salt dried at 200° gave 0.1758 gram $CaSO_4$.

	Calculated for $CaC_5HBrSO_6.$	Found. I.	Found. II.
Ca	12.94	12.76	12.83

Plumbic β-Sulpho-δ-brompyromucate, $PbC_5HBrSO_6.1\frac{1}{2}H_2O.$ — The lead salt is tolerably soluble in cold water, and its solubility is but little increased by heat. The salt dried by exposure to the air contains one and a half molecules of water, one molecule of which it retains when dried over sulphuric acid.

I. 1.5047 gram of the air-dried salt lost, at 150°, 0.0815 gram H_2O, and gave 0.9074 gram $PbSO_4$.

II. 1.7254 gram of the air-dried salt lost, at 150°, 0.0925 gram H_2O.

III. 0.5361 gram of the air-dried salt gave 0.3239 gram $PbSO_4$.

	Calculated for $PbC_5HBrSO_6.1\frac{1}{2}H_2O.$	I.	Found. II.	III.
H_2O	5.37	5.42	5.36	
Pb	41.15	41.20		41.27

1.6958 gram of the salt dried over sulphuric acid lost, at 150°, 0.0629 gram H_2O.

	Calculated for $PbC_5HBrSO_6.H_2O.$	Found.
H_2O	3.64	3.71

I. 0.5894 gram of the salt dried at 150° gave 0.3743 gram $PbSO_4$.

II. 0.6496 gram of the salt dried at 150° gave 0.4122 gram $PbSO_4$.

	Calculated for $PbC_5HBrSO_6.$	Found. I.	Found. II.
Pb	43.49	43.38	43.35

Argentic β-Sulpho-δ-brompyromucate, $Ag_2C_5HBrSO_6.2H_2O.$ — The silver salt is sparingly soluble in cold water, and crystallises in plates which contain two molecules of water.

1.3888 gram of the air-dried salt lost, at 115°, 0.0968 gram H_2O.

	Calculated for $Ag_2C_5HBrSO_6.2H_2O.$	Found.
H_2O	6.91	6.97

I. 0.1715 gram of the salt dried at 115° gave, on precipitation with HBr, 0.1340 gram AgBr.

II. 0.1725 gram of the salt dried at 115° gave, on precipitation with HBr, 0.1337 gram AgBr.

III. 0.4347 gram of the salt dried at 115° gave, on heating with HNO_3, 0.1684 gram AgBr and 0.2082 gram $BaSO_4$.

IV. 0.5100 gram of the salt dried at 115° gave, on heating with HNO_3, 0.1980 gram AgBr.

	Calculated for $Ag_2C_5HBrSO_6$.	I.	Found. II.	III.	IV.
Ag	44.54	44.88	44.53		
SO_3	16.50			16.44	
Br	16.50			16.49	16.52

Potassic β-Sulpho-δ-brompyromucate, $K_2C_5HBrSO_6$.—The potassium salt is very soluble in cold water, and crystallises in thick rhombic plates which are anhydrous.

I. 0.4510 gram of the salt gave 0.2247 gram K_2SO_4.

II. 0.5020 gram of the salt gave 0.2530 gram K_2SO_4.

	Calculated for $K_2C_5HBrSO_6$.	Found. I.	II.
K	22.52	22.37	22.62

Action of Bromine.

Bromine in aqueous solution acts with readiness upon β-sulpho-δ-brompyromucic acid or its salts. The products vary with the conditions chosen. If one molecule of bromine is slowly added to a cold aqueous solution of the barium salt, carbonic dioxide is evolved and baric dibromfurfuran sulphonate is formed together with baric bromide. This reaction is obviously identical with that noticed by Hill and Hartshorn[1] in the decomposition of δ-brompyromucic acid in alkaline solution by bromine in which αα-dibromfurfuran is formed. If the baric β-sulpho-δ-brompyromucate is suspended in a little water, and bromine slowly added, the salt at first dissolves, and soon after the baric dibromfurfuran sulphonate crystallises out. From a more dilute solution the salt can readily be obtained by evaporation. In the latter case the solution is but feebly acid and the yield nearly quantitative.

[1] Ber. **18**, 448.

Baric aa-Dibromfurfuran-β-sulphonate, $Ba(C_4HBr_2SO_4)_2.H_2O$.
—This salt is quite readily soluble in hot water, more sparingly in cold water, and crystallises in pearly scales or plates.

I. 0.8179 gram of the air-dried salt lost, at 135°, 0.0204 gram H_2O.

II. 0.8833 gram of the air-dried salt lost, at 125°, 0.0224 gram H_2O.

	Calculated for $Ba(C_4HBr_2SO_4)_2.H_2O$.	I.	Found. II.
H_2O	2.35	2.49	2.54

I. 0.3952 gram of the salt dried at 135° gave 0.1238 gram $BaSO_4$.

II. 0.3932 gram of the salt dried at 135° gave 0.1223 gram $BaSO_4$.

III. 0.4219 gram of the salt dried at 125° gave 0.1320 gram $BaSO_4$.

	Calculated for $Ba(C_4HBr_2SO_4)_2$.	I.	Found. II.	III.
Ba	18.40	18.42	18.28	18.40

Potassic aa-Dibromfurfuran-β-sulphonate, $KC_4HBr_2SO_4$. — The potassium salt can readily be made by the action of bromine upon a slightly alkaline solution of potassic β-sulpho-δ-brompyromucate. It crystallises in well formed prisms which are anhydrous.

I. 0.3725 gram of the salt gave 0.4090 gram $AgBr$, and 0.2540 gram $BaSO_4$.

II. 0.3329 gram of the salt gave 0.3649 gram $AgBr$, and 0.2283 gram $BaSO_4$.

	Calculated for $KC_4HBr_2SO_4$.	I.	Found. II.
Br	46.49	46.73	46.66
SO_3	23.25	23.41	23.55

Bromine in aqueous solution readily attacks the salts of the aa-dibromfurfuran-β-sulphonic acid ; so that, if an excess of bromine is added to a salt of β-sulpho-δ-brompyromucic acid, only the products of this second stage of the reaction are obtained. The oxidation goes on slowly at ordinary temperatures, more rapidly on warming, and even after treating for a long time at 100° with an excess of bromine, no appreciable amount of sulphuric acid is formed.   The final product of the reaction is an acid containing the sulpho-group, which we have named, provisionally at least, sulphofumaric acid.   The acid itself we found to be extremely soluble in water, and upon evaporating the aqueous solution *in vacuo*,

a viscous residue was obtained which did not crystallise even after long standing. The barium, lead, and silver salts of the acid were very sparingly soluble even in boiling water. The calcium and potassium salts, on the other hand, were very soluble even in cold water, and could not be obtained in crystalline form. As might have been expected, the strontium salt proved to be more readily soluble than the barium salt, but it did not crystallise well from water. We also found it impossible to prepare an acid salt the properties of which were more favorable to purification. We therefore prepared and analysed the barium and silver salts.

Baric Sulphofumarate, $Ba_3(C_4HSO_7)_2 . x\ H_2O$.—To an aqueous solution of baric β-sulpho-δ-brompyromucate we added a slight excess of bromine, and finished the reaction by the aid of heat. The strongly acid solution thus obtained was partially neutralised by the addition of baric carbonate, the carbonic dioxide expelled by long boiling, and baric hydrate then added to alkaline reaction. In this way a voluminous flocculent precipitate was thrown down, which was dissolved in boiling dilute hydrochloric acid and reprecipitated by ammonic hydrate. Although the baric sulphofumarate was markedly soluble in a solution of ammonic chloride, the analytical results were more satisfactory than when the salt was again precipitated by baric hydrate. The voluminous precipitate, when thoroughly washed and dried by exposure to the air, formed a light, porous hygroscopic mass, which gave us on analysis varying percentages. The salt dried at 130° gave, however, a constant percentage of barium corresponding to that required by a salt with three molecules of water, and even at 200° one molecule of water appeared to be retained. In each case, however, the ratio between the barium and sulphur was found to be as 3 to 2.

0.6486 gram of the air-dried salt gave, after fusion with Na_2CO_3 and $KClO_3$, 0.4918 gram $BaSO_4(Ba)$ and 0.3310 gram $BaSO_4(SO_3)$.

	Calculated for $Ba_3(C_4HSO_7)_2.7H_2O$.	Found.
Ba	44.52	44.58
SO_3	17.34	17.52
	$Ba : SO_3 = 2\ 97 : 2.$	

Here it will be seen that the air-dried salt contained seven molecules of water. This, however, must have been an accidental coincidence, since the same salt after several days further exposure to the air, contained more water.

1.2865 gram of the air-dried salt lost, at 200°, 0.1686 gram H_2O.

	Calculated for $Ba_3(C_4HSO_7)_2.7H_2O.$	Found.
$6H_2O$	11.70	13.10

0.5471 gram of the salt dried at 200° gave 0.4706 gram $BaSO_4(Ba)$, and 0.3159 gram $BaSO_4(SO_3)$.

	Calculated for $Ba_3(C_4HSO_7)_2.H_2O.$	Found.
Ba	50.42	50.56
SO_3	19.63	19.82

$$Ba : SO_3 = 2.98 : 2.$$

I. 1.1659 gram of the salt dried at 130° lost, at 200°, 0.0480 gram H_2O.

II. 0.4608 gram of the salt dried at 130° gave 0.3798 gram $BaSO_4$.

III. 0.5175 gram of the salt dried at 130° gave 0.4256 gram $BaSO_4$.

	Calculated for $Ba_3(C_4HSO_7)_2.3H_2O.$	I.	Found. II.	III.
$2H_2O$	4.23	4.12		
Ba	48.29		48.45	48.35

In the sulphuric acid determinations given above, the baric sulphate was precipitated in the presence of large quantities of sodium and potassium salts. Although it was purified in the usual way before weighing, the results are undoubtedly still somewhat too high.

Argentic Sulphofumarate, $Ag_3C_4HSO_7 . xH_2O$.—On adding a solution of ammonic sulphofumarate to an excess of argentic nitrate, the silver salt is thrown down as a heavy curdy precipitate, which frequently becomes crystalline on standing. It is very sparingly soluble in cold water, somewhat more readily in hot. The air-dried salt contains water, a part of which at least it loses at 100°. At 110° it loses more rapidly in weight, but decomposition ensues at the same time. A sample of the salt which had been dried for some time at 100°, but which was still losing very slowly in weight, was analysed with the following results:

I. 0.4448 gram of the salt gave 0.4673 gram AgBr, and 0.1933 gram $BaSO_4$.

II. 0.4834 gram of the salt gave 0.2933 gram Ag.

	Calculated for $Ag_3C_4HSO_7.H_2O.$	I.	Found. II.
Ag	60.54	60.39	60.67
SO_3	14.95	14.92	

$$Ag : SO_3 = 3.01 : 1.$$

The air-dried salt had already lost at 100° about one molecule of water.

1.0317 gram of the air-dried salt lost, at 100°, 0.0368 gram H_2O.

	Calculated for $Ag_3C_4HSO_7.2H_2O$.	Found.
$1 H_2O$	3.26	3.57

The air-dried salt, therefore, appeared to contain two molecules of water. The analysis of a second preparation of the air-dried salt gave substantially the same ratio between silver and sulphur, and yet showed that the salt contained a lower percentage of silver.

0.4680 gram of the air-dried salt gave 0.3561 gram AgCl and 0.2009 gram $BaSO_4$.

	Calculated for $Ag_3C_4HSO_7.2H_2O$.	Found.
Ag	58.59	57.28
SO_3	14.46	14.73

$$Ag : SO_3 = 2.88 : 1.$$

By drying over sulphuric acid the precipitated silver salt, we were unable to obtain it with any more definite or constant percentages of water.

The lead salt is almost insoluble in water or in dilute acetic acid; but we have been unable as yet to obtain any results on analysis which were wholly satisfactory.

There can be no doubt that β-sulpho-δ-brompyromucic acid is decomposed by bromine in aqueous solution according to the following equations:

$$C_5H_3BrSO_6 + Br_2 = C_4H_2Br_2SO_4 + CO_2 + HBr.$$
$$C_4H_2Br_2SO_4 + Br_2 + 3H_2O = C_4H_4SO_7 + 4HBr.$$
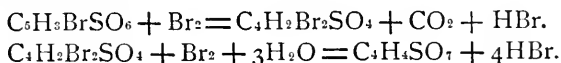
Action of Nitric Acid.

The decomposition of β-sulpho-δ-brompyromucic acid with nitric acid we have followed qualitatively. We have been unable hitherto to effect a replacement of the sulpho-group by the action of fuming nitric acid, as we had so readily done with the δ-sulphonic acids. In this case, whatever was the strength of the nitric acid, we could only prove the formation of an acid which was identical in its behavior with sulphofumaric acid. Not unfrequently, however, the oxidation had gone further, and oxalic acid was also formed together with sulphuric acid.

We have made a few experiments concerning the action of fusing potassic hydrate upon potassic β-sulpho-δ-brompyromucate, and have as yet been able to prove the formation of nothing but oxalic acid. While it is doubtful whether any other product but oxalic acid is normally formed, we shall study the reaction further, as well as the action of fusing sodic formiate.

β-SULPHOPYROMUCIC ACID.

The ammoniacal solution β-sulpho-δ-brompyromucic acid is reduced without difficulty by zinc dust. A strongly ammoniacal solution of the barium salt was heated for some time with an excess of zinc dust, the filtered solution boiled with the addition of baric hydrate till ammonia was no longer given off, and the excess of baric hydrate precipitated with carbonic dioxide. The solution thus obtained yielded on evaporation the barium salt of β-sulpho-pyromucic acid in satisfactory quantity. Since this salt was very nearly if not quite as soluble in cold water as in hot, its purification could most conveniently be effected by conversion into the acid salt, which was readily soluble in hot water, but sparingly in cold water.

Baric β-Sulphopyromucate, $BaC_5H_2SO_6 . 3 H_2O$.—This salt is sparingly soluble in hot water, and the hot saturated solution deposits nothing on cooling. By evaporation *in vacuo* over sulphuric acid, the salt is obtained in clear, obliquely terminated plates which contain three molecules of water.

I. 1.5356 gram of the air-dried salt lost, at 160°, 0.2156 gram H_2O.

II. 1.2179 gram of the air-dried salt lost, at 160°, 0.1707 gram H_2O.

III. 0.7448 gram of the air-dried salt gave 0.4571 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_6.3H_2O$.	I.	Found. II.	III.
H_2O	14.18	14.05	14.02	
Ba	35.96			36.08

I. 0.7139 gram of the salt dried at 160° gave 0.5092 gram $BaSO_4$.
II. 0.7303 gram of the salt dried at 160° gave 0.5197 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_6$.	Found. I.	II.
Ba	41.90	41.94	41.84

If the solution is evaporated at 100°, the salt separates in small clear prisms with oblique truncations, which appear to contain one molecule of water.[1] If the salt is removed while the solution is hot, it contains a somewhat lower percentage of water (IV) than it does when the solution is first allowed to cool (I, II, and III). In the latter case it undoubtedly contains a slight admixture of the salt containing three molecules of water.

I. 4.2755 grams of the air-dried salt lost, at 165°, 0.2510 gram H_2O.

II. 2.1345 grams of the air-dried salt lost, at 165°, 0.1290 gram H_2O.

III. 0.5901 gram of the air-dried salt gave 0.3981 gram $BaSO_4$.

IV. 0.8840 gram of the air-dried salt lost, at 160°, 0.0484 gram H_2O.

	Calculated for $BaC_5H_2SO_6.H_2O$.	I.	II.	III.	IV.
				Found.	
H_2O	5.22	5.87	6.04		5.47
Ba	39.71			39.66	

I. 0.6005 gram of the salt dried at 165° gave 0.4270 gram $BaSO_4$.

II. 0.6010 gram of the salt dried at 165° gave 0.4269 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_6$.	I.	II.
		Found.	
Ba	41.90	41.79	41.76

In determining the solubility of the barium salt in cold water, we evaporated its solution rapidly until crystals began to appear, and then cooled with constant stirring. Abundant crystals of the salt were thus formed. In order to satisfy ourselves that solutions of constant composition could be obtained in this way, we made four separate determinations.

I. 16.2601 grams of the solution saturated at 21° gave 0.2172 gram $BaSO_4$.

II. 14.4321 grams of the solution saturated at 21° gave 0.1950 gram $BaSO_4$.

III. 12.1256 grams of the solution saturated at 21° gave 0.1646 gram $BaSO_4$.

IV. 12.7701 grams of the solution saturated at 21° gave 0.1788 gram $BaSO_4$.

The aqueous solution of barium salt saturated at 21°, therefore, contained the following percentages of the anhydrous salt :

[1] In a preliminary paper (Ber. **18,** 2095) the baric β-sulphopyromucate was described as containing but one molecule of water. At that time the salt obtained by evaporation at 100° had alone been analysed.

	I.	II.	III.	IV.
	1.88	1.90	1.91	1.96

Acid Baric β-Sulphopyromucate, $Ba(C_5H_3SO_6)_2 \cdot 3H_2O$.—This salt may be made by dissolving the neutral barium salt in hydrochloric acid, or, more advantageously, by mixing solutions of the neutral barium salt and the free acid in equivalent quantities. It is readily soluble in hot water, more sparingly in cold water, and crystallises in small, obliquely truncated prisms which are permanent in the air.

I. 1.4255 gram of the air-dried salt lost, at 130°, 0.1403 gram H_2O.

II. 1.3386 gram of the air-dried salt lost, at 135°, 0.1271 gram H_2O.

III. 0.5371 gram of the air-dried salt gave 0.2193 gram $BaSO_4$.

	Calculated for $Ba(C_5H_3SO_6)_2 \cdot 3H_2O$.	I.	Found. II.	III.
H_2O	9.42	9.84	9.49	
Ba	23.91			24.00

0.3068 gram of the anhydrous salt gave 0.1378 gram $BaSO_4$.
II. 0.3128 gram of the anhydrous salt gave 0.1409 gram $BaSO_4$.

	Calculated for $Ba(C_5H_3SO_6)_2$.	I.	Found. II.
Ba	26.39	26.41	26.48

Calcic β-Sulphopyromucate, $CaC_5H_2SO_6 \cdot 2H_2O$.—The calcium salt is quite readily soluble in cold water, and separates on evaporation in crusts. By the addition of alcohol to a cold aqueous solution the salt is precipitated in the form of small prisms, which, when dried by exposure to the air, contain two molecules of water.

I. 1.0454 gram of the air-dried salt lost, at 130°, 0.1444 gram H_2O.

II. 1.0285 gram of the air-dried salt lost, at 135°, 0.1415 gram H_2O.

	Calculated for $CaC_5H_2SO_6 \cdot 2H_2O$.	I.	Found. II.
H_2O	13.53	13.81	13.74

I. 0.4790 gram of the anhydrous salt gave 0.2825 gram $CaSO_4$.
II. 0.4118 gram of the anhydrous salt gave 0.2425 gram $CaSO_4$.

	Calculated for $CaC_5H_2SO_6$.	I.	Found. II.
Ca	17.40	17.35	17.32

Potassic β-Sulphopyromucate, $K_2C_5H_2SO_6.2\frac{1}{2}H_2O$.—The potassium salt is extremely soluble in water, and crystallises in long prisms. It separates in the form of fine needles on the addition of alcohol to its aqueous solution.

1.2358 gram of the air-dried salt lost, at 140°, 0.1788 gram H_2O.

	Calculated for $K_2C_5H_2SO_6.2\frac{1}{2}H_2O$.	Found.
H_2O	14.37	14.47

I. 0.4028 gram of the salt dried at 140° gave 0.2601 gram K_2SO_4.

II. 0.4120 gram of the salt dried at 140° gave 0.2665 gram K_2SO_4.

	Calculated for $K_2C_5H_2SO_6$.	I.	Found. II.
K_2	29.16	28.99	29.04

Action of Bromine.

We have as yet made but few experiments as to the action of bromine in aqueous solution upon β-sulphopyromucic acid. They have only been sufficient to show that oxidation here follows the same course that it does in the case of other derivatives of pyromucic acid in which the δ-hydrogen atom is unreplaced. At first products are formed which reduce silver energetically in ammoniacal solution; and only after long warming with an excess of bromine is an acid obtained which resembles in its behavior sulphofumaric acid. Three molecules of bromine gave an acid whose barium salt was very readily soluble in water, and which reduced silver on heating. This reaction will be studied more carefully hereafter, with the hope of isolating the aldehyde acid which is doubtless formed.

ACTION OF FUMING SULPHURIC ACID UPON βδ-DIBROMPYRO-MUCIC ACID.

By the action of fuming sulphuric acid upon δ-brompyromucic acid, we obtained a sulphonic acid which of necessity contained its sulpho-group either in the β or in the γ position. Analogy left little room for doubt that the acid thus formed was in fact a β-sulphonic acid. It seemed to us not impossible that a γ-sulphonic acid could be formed by the action of fuming sulphuric acid upon

$\beta\delta$-dibrompyromucic acid, which still retains its γ-hydrogen atom. We found, however, that the reaction takes quite a different course, and that no sulphonic acid is formed.

Pure dry $\beta\delta$-dibrompyromucic acid, melting at 167°–168°, was slowly added to several times its weight of fuming sulphuric acid. No visible reaction took place, and after twenty-four hours standing, water precipitated the acid apparently quite unchanged. After the lapse of several days decomposition set in, and carbonic dioxide, bromine, hydrobromic acid, and sulphurous dioxide were evolved. So slow was the reaction that two or three weeks were necessary for its completion at ordinary temperatures. When water gave only a slight flocculent precipitate, the bromine was expelled as far as possible with a current of air, and the whole diluted with water. The small quantity of insoluble matter was then removed by filtration, and the aqueous solution thoroughly extracted with ether. The ether left on distillation a white crystalline acid which, when pressed and dried, melted at 127°–128°. The quantity of the acid thus obtained was about half that of the $\beta\delta$-dibrompyromucic acid taken. The acid dissolved readily in less than its own weight of water, leaving but the slightest turbidity, and on evaporation it crystallised in colorless prisms which melted at 129°–130°.[1] An analysis showed this substance to be monobrommaleic acid.

0.2235 gram of the acid dried over sulphuric acid gave 0.2161 gram AgBr.

Calculated for $C_4H_3BrO_4$.	Found.
41.03	41.15

[1] The melting point of monobrommaleic acid is usually given as 128°, and I have frequently determined it myself without noticing that it varies greatly with the time of heating, as is the case with dibrommaleic acid. How great this variation may be can be seen from the following observations, which I made with this one analysed sample. The acid in thin-walled capillary tubes was dipped into the bath heated to constant temperature, and the time of melting noted.

Temperature of bath.	Minutes before melting.
143°	0 17
140	0.5
135	0.83
133	1.3
131	1.5
125	4.5
121	8.0

The melting point, 129°–130°, given above was the result of two successive attempts to determine it at the ordinary speed.—H. B. H.

The melting point and the complete and ready solubility of the crude product showed that monobrommaleic was the only essential constituent. The aqueous solution from which the monobrommaleic acid had been extracted with ether was warmed to expel the ether dissolved, neutralised with baric carbonate, and the filtered solution evaporated. A careful examination of the small amount of barium salt thus obtained failed to show that even a trace of a sulphonic acid had been formed.[1] This result is in accordance with the results of Hill and Sanger,[2] who found that the γ-hydrogen of the $\beta\delta$-dibrompyromucic acid could not be replaced by bromine.

Action of Fuming Sulphuric Acid upon Tribrompyromucic Acid.

After the experiments just described, there could be little doubt as to the action of fuming sulphuric acid upon tribrompyromucic acid. We thought it worth while, however, to make a single experiment in this direction. Tribrompyromucic acid dissolved readily in fuming sulphuric acid, and decomposition quickly ensued at ordinary temperatures, so that the reaction was completed in the course of a day or two. The diluted solution yielded, as the only product of the reaction, dibrommaleic acid, which we recognised by the melting point of its anhydride ($114°$–$115°$), and by the analysis of its barium salt.

0.5812 gram of the air-dried salt gave 0.3063 gram $BaSO_4$.

	Calculated for $BaC_4Br_2O_4.2H_2O$.	Found.
Ba	31.78	31.98

Theoretical Considerations.

The constitution of the various substances described in the preceding pages requires but little discussion. The position of the sulpho-group in the δ-sulphopyromucic acid is established not only by the formation of fumaric acid by its oxidation, but also still more conclusively by its formation in the reduction of $\beta\gamma$-dibrom-δ-sulphopyromucic acid, to which of necessity the formula

[1] The statement made in a preliminary paper (Ber. **18**, 2095), that a sulphonic acid was formed in this reaction, was subsequently proved to be incorrect.

[2] Proceedings, Amer. Acad. **21**, 175.

$$BrC = C - COOH$$
$$| \qquad \searrow O$$
$$| \qquad \nearrow$$
$$BrC = C - SO_2OH$$
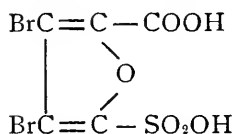
must be assigned. The close resemblance in structure of this acid to dehydromucic acid,

$$HC = C - COOH$$
$$| \qquad \searrow O$$
$$| \qquad \nearrow$$
$$HC = C - COOH,$$
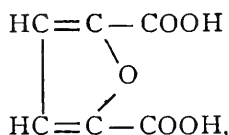
is evident, and the formation of δ-nitropyromucic acid from dehydromucic acid as observed by Klinkhardt,[1] finds its complete parallel in the conversion of this sulphonic acid by the action of nitric acid into $\beta\gamma$-dibrom-δ-nitropyromucic acid and $\alpha\alpha$-dinitro-$\beta\beta$-dibromfurfuran.

$$BrC = C - COOH \qquad\qquad BrC = C - NO_2$$
$$| \qquad \searrow O \qquad\qquad\qquad | \qquad \searrow O$$
$$| \qquad \nearrow \qquad\qquad\qquad\qquad | \qquad \nearrow$$
$$BrC = C - NO_2 \qquad\qquad BrC = C - NO_2.$$
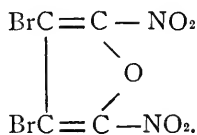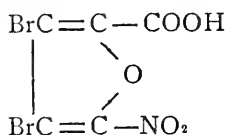
There can be no doubt that the neutral substance formed by the action of fuming nitric acid upon δ-sulphopyromucic acid at the same time with the δ-nitropyromucic acid is $\alpha\alpha$-dinitrofurfuran.

$$HC = C - COOH \qquad\qquad HC = C - NO_2$$
$$| \qquad \searrow O \qquad\qquad\qquad | \qquad \searrow O$$
$$| \qquad \nearrow \qquad\qquad\qquad\qquad | \qquad \nearrow$$
$$HC = C - NO_2 \qquad\qquad HC = C - NO_2.$$
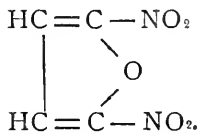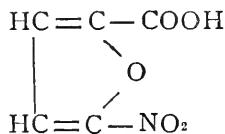
The structure of the β-brom-δ-sulphopyromucic acid is determined by its reduction to δ-sulphopyromucic acid, and by its formation from β-brompyromucic acid, the constitution of which has been established by Hill and Sanger.[2] The sulphonic acid and the nitro-acid formed from it must be

$$BrC = C - COOH \qquad\qquad BrC = C - COOH$$
$$| \qquad \searrow O \qquad\qquad\qquad | \qquad \searrow O$$
$$| \qquad \nearrow \qquad\qquad\qquad\qquad | \qquad \nearrow$$
$$H - C = C - SO_2OH \qquad\qquad HC = C - NO_2.$$
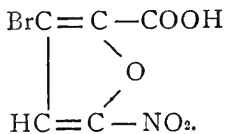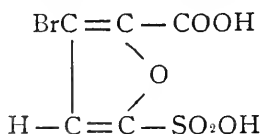
[1] J. prakt. Chem. N. F. **25**, 41.   [2] Proceedings, Amer. Acad. **21**, 181.

Concerning the structure of the sulphonic acid formed from δ-brompyromucic acid, it is impossible to draw conclusions equally definite. When we bear in mind, however, the fact that bromine, like sulphuric acid, first replaces the δ-hydrogen atom of the pyromucic acid, and in acting upon the δ-brompyromucic acid thus formed the β-hydrogen alone can further be replaced by bromine, there seems no reasonable doubt that the sulphuric acid in acting upon δ-brompyromucic acid also replaces by the sulpho-group the β-hydrogen atom. This view is still further confirmed by the fact that the γ-hydrogen atom of the βδ-dibrompyromucic acid seems incapable of such replacement. If this view be correct, the sulphonic acid in question has the form

$$HOSO_2C = C - COOH$$
$$\Big| \qquad \diagdown O$$
$$\Big| \qquad \diagup$$
$$HC = CBr.$$
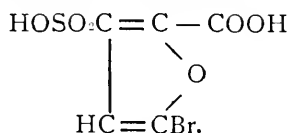
In any case, the αα-dibromfurfuran-β-sulphonic acid formed from it by the action of bromine has the structure

$$HOSO_2C = CBr$$
$$\Big| \qquad \diagdown O$$
$$\Big| \qquad \diagup$$
$$HC = CBr.$$
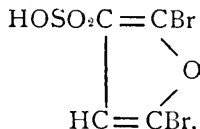
ON THE OCCURRENCE OF ARSENIC IN GLASS AND IN THE CAUSTIC ALKALIES,

With an Examination of the Action of the Strong Acids, Caustic Alkalies, and Other Reagents, upon Arsenical Glass.

By John Marshall and Charles S. Potts.

Over forty years ago the Academy of Medicine of Paris, at the request of the French Government, undertook the investigation of the occurrence of arsenic in glass, and as a result of the research declared that "the glass which they examined contained no arsenic, and although arsenic is sometimes used in glassmaking, and a

trace of it may be retained in some opaque glasses or enamels, it cannot be detected by any process of analysis in any of the clear glass met with in commerce, *all of the arsenic being volatilised during the manufacture of the glass.*"[1]

It is well known that arsenious oxide is extensively used in the manufacture of glass, principally to decompose the sodium sulphide formed in the process,[2] and also to effect the removal of color from the glass mixture containing carbon or silicate of iron. The arsenious oxide is reduced to the metallic form by the carbon and ferrous oxide at a dull red heat, and according to Wagner[3] and others, the *arsenic is volatilised.* Further on, however, Wagner (p. 392) states that in the use of arsenic in glassmaking, it should not be overlooked that a small portion of the arsenic remains in the finished glass as calcium arsenite or arseniate.

For some years past the presence of traces of arsenic in glass has been admitted. Lately, W. Fresenius[4] has determined it to be present in considerable quantity in some samples of Bohemian glass tubing, such as is used in many laboratory operations. In one of the three samples he found as much as 0.2 per cent. of arsenic. Again, M. Kreusler[5] found in a sample of Thuringian glass 0.15 per cent. of As_2O_3. In a sample of Bohemian combustion tubing the same investigator found 0.12 per cent. of As_2O_3, and in an easily fusible potash glass 0.10 per cent. of As_2O_3. The finding of arsenic in such quantity disproves the old belief that *all the arsenic is volatilised.* Upon inquiry at a glass bottle manufactory in Philadelphia, it was learned that in the process employed in the establishment, approximately twenty pounds of arsenious oxide were used to each melting of four thousand pounds of glass, and in making clear glass the pots were kept closed with a lid, thus in a measure preventing the escape of any arsenic that might volatilise.

The following investigation was begun primarily to determine the presence of arsenic in glass of American manufacture, but its scope was somewhat enlarged and glass of foreign make was included. The action of the caustic alkalies, strong acids, and ordinary laboratory reagents, upon the arsenical glass of the bottles in which they were contained, was also studied. The occurrence of arsenic in commercial caustic soda, sodium carbonate, and also

[1] Annales d'Hyg. Pub. et de Med. **11**, 224.   [2] Post. Chemische Technologie **2**, 17.
[3] Handbuch d. chem. Tech. 1886, 392.   [4] Ztschr. anal. Chem. **22**, 397.
[5] Wagner, Handbuch d. chem. Tech. 1886, 386.

in sodium hydrate and sodium carbonate sold as chemically pure, was investigated. In every case the presence of arsenic was first determined qualitatively by Marsh's test, and when found, a quantitative determination followed. In examining the glass for arsenic the following method was employed : The glass was pulverised in an agate mortar, then mixed with sodium carbonate, and fused. The fused mass was broken up and dissolved in water, then acidified with sulphuric acid, the separated silica filtered off, and the filtrate placed in the Marsh apparatus.

The reagents employed, sodium carbonate, sulphuric acid, and zinc, were tested in long continued control experiments and found to be perfectly free from arsenic. Lead was found in some of the samples of glass, but no quantitative determinations were made.

In the quantitative estimations the glass was pulverised as before and fused with sodium carbonate. The fused mass was broken up, dissolved in water, and acidified with sulphuric acid. The silica was filtered off, and the filtrate, to which had been added a solution of sulphurous acid gas, was evaporated to a small volume on a water-bath, and then diluted with a little hot water and filtered from the remaining separated silica. Through the warm filtrate a washed stream of hydrogen sulphide was passed for several hours, and the precipitated arsenious sulphide collected on a filter paper and washed. The precipitate was then dissolved, while on the filter, with a few drops of dilute ammonium hydrate, the solution evaporated to dryness, and the residue warmed with strong nitric acid until the sulphide was completely oxidised. The acid was driven off by evaporation to dryness, and the residue was warmed with a little water and then filtered. Magnesium mixture was added to the filtrate and the whole allowed to stand twenty-four hours. The precipitated magnesium ammonium arseniate was collected on a filter paper and the arsenic weighed as magnesium pyro-arseniate.

	Quantity of glass employed.		Description.	Where made.	Amount of $Mg_2As_2O_7$ obtained.	Equivalent percentage of As_2O_3.
I	5.0 grams		8-liter bottle	Germany	0.010	0.127
II	5.0	"	Reagent bottle	Philadelphia	0.015	0.191
III	5.0	"	Beaker	"	0.024	0.306
IV	2.0	"	Reagent bottle	"	0.008	0.255
V	2.0	"	Refractory tubing	Thuringia	0.003	0.095
VI	5.0	"	8-liter bottle	Germany	0.008	0.102
VII	5.0	"	Beaker	Philadelphia	0.035	0.446

When glass tubing No. 5, which contained arsenic, but no lead, was used as a reduction tube and pure hydrogen passed through in Marsh's test, the brown coloration referred to by Fresenius[1] as produced directly at the point in contact with the flame invariably appeared.

Examination of the Caustic Alkalies, the Strong Acids and other Reagents, for the Presence of Arsenic, and Investigation of their Solvent Action upon the Arsenical Glass of the Bottles in which they were contained.

In testing the alkalies, sulphuric acid was used for acidifying. The strong acids were sufficiently diluted with distilled water, or partly neutralised with sodium carbonate before testing.

In all but one of the samples of caustic soda examined, arsenic was found, varying from a trace to quite a considerable percentage. Four samples of caustic potash were examined, but no arsenic was detected.

Qualitative.

I. Two samples, each containing twenty grams of sodium carbonate, sold as chemically pure and obtained from different German makers, separately neutralised with sulphuric acid and tested in Marsh's apparatus, gave different results. One sample furnished a very slight mirror, the other gave no indication of the presence of arsenic.

II. Ten grams of sodium hydrate, in sticks made in Philadelphia, gave a slight mirror. These sticks were contained in an arsenical glass bottle, so that care was taken to select the sticks not in direct contact with the glass. The end in contact with the bottom or side of the bottle was broken off and rejected.

III. Ten grams of caustic soda, made by the Solvay process, failed to show the presence of arsenic.

Quantitative.

In estimating the quantity of arsenic in the alkalies, they were dissolved in water, then rendered slightly acid with sulphuric acid, sulphurous acid added, and the latter driven off by heating the liquid. Hydrogen sulphide was passed through the solution, the precipitated arsenious sulphide was collected on a filter, washed,

[1] Ztschr. anal. Chem. **22**, 400.

dissolved in ammonium hydroxide, the solution evaporated to dryness, and the residue of arsenious sulphide oxidised with nitric acid. The nitric acid was driven off by heat, the residue dissolved in water, filtered, magnesium mixture added to the filtrate, the precipitate was collected on a filter, and the arsenic weighed as pyro-arseniate.

I. One hundred grams of sodium hydrate in sticks, made by a Philadelphia firm, furnished 0.0044 gram of $Mg_2As_2O_7$, equivalent to 0.0028 per cent. of As_2O_3.

II. Three grams of a very white caustic soda, sold as chemically pure, gave 0.004 gram of $Mg_2As_2O_7$, equivalent to 0.0848 per cent. of As_2O_3.

III. Ten grams of another sample of white caustic soda, represented to be chemically pure, yielded 0.0062 gram of $Mg_2As_2O_7$, equivalent to 0.039 per cent. of As_2O_3.

IV. Twenty grams of a sample of " crude carbonated soda," made in England, furnished 0.021 gram of $Mg_2As_2O_7$, equivalent to 0.067 per cent. of As_2O_3.

In order to study the solvent action of caustic soda upon glass, bottles of arsenical glass of about 500 cc. capacity were filled with a 10 per cent. solution of sodium hydroxide (free from arsenic) and allowed to stand different periods of time.

I. 20 cc. of the solution which had been allowed to stand in a bottle five months, when tested with Marsh's test, produced a very strong mirror in six minutes.

II. 20 cc. of the solution contained in a bottle one month gave a decided mirror in ten minutes.

III. 20 cc. of the solution which had been kept in a bottle twenty-three hours gave no reaction. Twenty cubic centimetres of this solution were tested after the lapse of every twenty-three hours, and no arsenical mirror appeared until the sixty-ninth hour.

IV. 20 cc. of a 10 per cent. solution of potassium hydroxide kept in a bottle twenty-four hours readily produced an arsenical mirror.

The strong acids, sulphuric and hydrochloric, which were examined had been kept in large (eight-liter) arsenical glass bottles for different lengths of time. The bottles being of large size, quite an extensive surface of glass was exposed to the action of the acid. The acids, previously neutralised with sodium carbonate (free from arsenic), were tested in Marsh's apparatus.

I. 40 cc. of strong hydrochloric acid (American), kept in an arsenical glass bottle three months, gave no trace of arsenic.

II. 40 cc. of strong hydrochloric acid (German), contained in an arsenical glass bottle three years, failed to give a trace of arsenic. The glass of the bottle in which this acid was kept contained 0.102 per cent. of As_2O_3.

III. 40 cc. of strong sulphuric acid (American), contained in an arsenical glass bottle three months, did not give a trace of arsenic.

IV. 40 cc. strong sulphuric acid (German), contained in an arsenical glass bottle six years, failed to give any indication of arsenic. The glass of this bottle contained 0.127 per cent. of As_2O_3.

Some of the ordinary laboratory reagents kept in arsenical glass bottles were tested with Marsh's test, but, as shown below, failed to give any indication of the presence of arsenic.

Two samples, 50 cc. each, of ammonium hydroxide, kept respectively one and two months, failed to show arsenic. Solutions of potassium nitrate and chlorate and a strong solution of barium chloride kept in arsenical glass bottles, failed to produce a mirror.

Sodium carbonate, which originally contained arsenic, was after several recrystallisations found to be entirely free from the metal.

It will be observed that every sample of clear glass examined except one, and all the caustic soda except one sample (that made by the Solvay process), contained arsenic. The caustic potash, ammonium hydroxide, and the common reagents examined were found to be free from arsenic. The strong acids, ammonium hydroxide, and ordinary reagents had no dissolving action upon the surface of arsenical glass bottles, whereas solutions of the fixed alkalies had such solvent action.

Chemical Laboratory, Medical Department, University of Pennsylvania.

NOTE ON THE BUTINES.

By L. M. Norton and A. A. Noyes.

There are certainly four possible hydrocarbons of the composition C_4H_6: dimethylacetylene, CH_3—$C{\equiv}C$—CH_3; ethylacetylene, $CH{\equiv}C$—C_2H_5; vinylethylene, $CH_2{=}CH$—$CH{=}CH_2$; and methylisoallylene, CH_3—$CH{=}C{=}CH_2$. The first three of these have already been prepared. Vinylethylene was first obtained by

Caventou[1] in 1863, by the action of heat on amyl alcohol, and it has since been many times prepared by numerous other investigators. Its production from erythrite by reduction,[2] the identity of its tetrachloride with that prepared by the action of phosphorus pentachloride on erythrite,[3] and its oxidation to formic acid,[4] fully establish its constitution. Ethylacetylene was first obtained by Bruylants[5] in 1875, from methylethyldichlormethane and alcoholic potash. Its behavior toward ammoniacal cuprous and silver solutions shows it to be a derivative of acetylene formed by the replacement of only one hydrogen atom. Dimethylacetylene has been prepared by Lermontoff by the action of alcoholic potash on pseudo-butylene bromide, and treatment of the brombutylene obtained with sodium ethylate; for by contact with sulphuric acid, the butine so prepared polymerises to hexamethylbenzene.[6] The fourth butine, methylisoallylene, was the subject of this investigation.

The method used for its preparation consisted in the reduction of butyric chloral, $CH_3 — CHCl — CCl_2 — CHO$, to the corresponding alcohol by addition of zinc ethyl, and subsequent decomposition of the zinc compound by water as recommended by Garzarolli.[7] The hydroxyl of this alcohol was then replaced by chlorine by means of phosphorus pentachloride, giving methylisoallylene tetrachloride, $CH_3 — CHCl — CCl_2 — CH_2Cl$, from which, to obtain the butine, it was only necessary to remove the chlorine by the action of the zinc-copper couple and alcohol. That the butyric chloral has the constitution assigned to it above has been proved by Friedrich,[8] who showed the identity of the reduction product of its corresponding acid with α-chlorcrotonic acid, and by Lieben and Zeisel,[9] who prepared it by the condensation of aldehyde with chloraldehyde, and who found that the dichlorpropylene split from it by caustic potash gave acetic acid on oxidation. That the atoms undergo no change in position in the reduction of the chloral to trichlorbutyl alcohol is evident, since both these substances give the same trichlorbutyric acid on oxidation.[10]

The butyric chloral used was obtained from commercial croton

[1] C. R. **56**, 646, 712.
[2] Henninger, Bull. Soc. chim. [2] **19**, 145; Ciamician and Magnaghi, Ber. **19**, 569.
[3] Henninger, Bull. Soc. chim. [2] **34**, 195.　　[4] Armstrong and Miller, J. Chem. Soc. **49**, 82.
[5] Ber. **8**, 412.　　[6] Almedingen, Ber. **14**, 2073.
[7] Ann. Chem. (Liebig) **213**, 369.　　[8] Ann. Chem. (Liebig) **219**, 371.
[9] Monatsh. Chem. **4**, 531.　　[10] Ann. Chem. (Liebig) **213**, 374.

chloral hydrate by distillation with sulphuric acid, and subsequent rectification over quicklime. It boiled from 163° to 167°. This was slowly added, in calculated quantity, to a mixture of equal parts of ether and zinc ethyl, placed in a flask filled with carbonic acid, and sealed by a delivery tube dipping under mercury. The temperature was not allowed to rise above that of the room. After the chloral was all added, the flask was allowed to stand for some hours, in order that the action might become complete, and the zinc compound was then decomposed by addition, in small portions, to water acidified with hydrochloric acid. A colorless oil was thus obtained which solidified after standing a short time. The trichlorbutyl alcohol crystallised from ether in large monoclinic prisms; it melted at 57° after one crystallisation. A yield of 60 to 70 per cent. was the result in several experiments.

The trichlorbutyl alcohol was now heated for several hours on a sand-bath in a flask provided with a return cooler with a slight excess of phosphorus pentachloride. The product was treated with water to remove the chlorides of phosphorus, distilled with steam, dried with calcium chloride and fractionated under reduced pressure. In this way methylisoallylene tetrachloride was obtained as a colorless liquid identical in properties with that prepared by Garzarolli in the same way. Cooled to —15° it showed no signs of solidification. The yield in four different cases was between 30 and 40 per cent.

The small yield in methylisoallylene tetrachloride is explained by the formation of a considerable quantity of $a_2\beta$-trichlorbutyl phosphate by the action of phosphorus oxychloride on the alcohol. This substance remained in the flask as a gelatinous mass on distilling with steam, and was purified by repeated crystallisations from alcohol. It separated from this solvent on spontaneous evaporation in slender colorless needles, which unite to radiated tufts if the crystallisation is rapid. The melting point is 85.3° to 85.4°. It gave the following results on analysis:

	Found.	Calculated for $(C_4H_6Cl_3O)_3PO$.
Carbon	24.39	24.98
Hydrogen	3.25	3.12
Chlorine	55.73	55.42
Phosphorus	4.91	5.38

In order to separate the chlorine from methylisoallylene tetrachloride, the latter was mixed in a flask with an equal volume of

alcohol, and the calculated quantity of the zinc-copper couple added.[1] The action begins of itself and must be checked by cooling the flask. The butine, after passing through a return cooler surrounded by water at 30°, was condensed by means of a mixture of ice and salt. It was entirely freed from alcohol by several fractionations. The yield is quite satisfactory.

Methylisoallylene is a colorless liquid, having the characteristic alliaceous odor of the hydrocarbons of the acetylene series. It boils constantly at 18°–19°. It gives no precipitate with ammoniacal cuprous chloride solution. The relation of carbon to hydrogen was found by combustion as follows:

	Found.		Calculated for C_4H_6.
	I.	II.	
Carbon	88.58	88.52	88.89
Hydrogen	11.42	11.48	11.11

Methylisoallylene unites with bromine, giving a liquid dibromide, which, however, takes up more bromine quite rapidly at the ordinary temperature, and therefore was not prepared in a state of purity. The tetrabromide, unlike those of vinylethylene and ethylacetylene, is a colorless liquid, which on cooling to —17° becomes less fluid but does not solidify.

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I.—SOME MODIFICATIONS OF THE METHODS OF ORGANIC ANALYSIS BY COMBUSTION.

BY WM. L. DUDLEY.

The investigations recorded here were undertaken with the hope that the method of ultimate organic analysis by combustion might be so modified as to be more rapid and none the less accurate.

The time required in preparation for the combustion by ordi-

[1] Gladstone and Tribe, J. Chem. Soc. **27**, 406. Armstrong and Miller, J. Chem. Soc. **49**, 82.

nary methods is much greater than that for the operation itself; it being consumed in drying and mixing materials, filling and heating up the tube, and in case several combustions are to be made at once, the time required in cooling the tube is very considerable. Then again the liability of loss by breaking the tube in heating and cooling is of no little importance.

The method of burning the substance with a current of air or oxygen in a glass combustion tube containing copper oxide is well known. It is stated, however, without satisfactory reason,[1] that the discrepancy in the hydrogen determination is as great in this method as in that where the substance and copper oxide are mixed, even though in the former the copper oxide is kept hot and the substance introduced in a boat. Kopfer[2] has described a method in which he employs platinum-black mixed with freshly ignited asbestos, instead of copper oxide; and to prevent the gases from passing through the tube without decomposition, he interposes three plugs of asbestos wound with fine platinum wire. The method is said to give very accurate results under careful management.

The platinum combustion tube which is being so generally used in carbon determinations in iron, has, as far as I am aware, never before been used in organic analysis, and the method which I shall describe here can be used with a glass as well as a platinum tube, although the description will be confined to the latter, as it is much preferred. Fig. 1 shows a section of the platinum tube which is

Fig. 1.

used in this laboratory, the main body of which is 48.5 cm. long and 1.5 cm. in diameter. The tail D is 13 cm. long and 0.5 cm. in diameter. The tube is filled from one third to one half full with manganese oxide in a coarse granulated condition, several lumps, too large to pass through the tail D, being put in first. The manganese oxide is prepared as follows: Manganous carbonate is decomposed with moderately dilute nitric acid in the cold, and evaporated to dryness. The residue is heated to redness over a blast lamp until all of the nitrate is decomposed. The mass, which is for the most part the oxide Mn_2O_3, is cooled and easily granu-

[1] Lieben, Ann. Chem. (Liebig), **187**, 142.   [2] J. Chem. Soc. **29**, 660.

lated to any degree of fineness. No channel is left in the tube, as the manganese oxide should be coarse enough to allow the products of combustion to pass with sufficient freedom. If a glass tube be used, a slight channel should be left. The substance is introduced in a porcelain or platinum boat[1] *B*, and followed by a roll of platinum gauze *C*, 3.5 cm. long, which has a loop in front so that it can be easily withdrawn. At *E* a gas-tight brass coupling is inserted; this carries a tube 0.5 cm. in diameter, to which is connected the apparatus furnishing either air or oxygen as desired.

Instead of the size of the tube being reduced to 0.5 cm. in the tail *D*, Fig. 1, the design shown in Fig. 2 is proposed to facilitate the passage of the water into the calcium chloride tube. The tube *B* is only slightly smaller than the main body, and the end is closed with a stopper carrying the stem of the calcium chloride tube. At *A* is placed a platinum basket to retain the manganese oxide.

FIG. 2.

The whole plan of the apparatus is shown in Fig. 3. Before introducing the substance, and connecting the calcium chloride tube and potash bulb, the portion of the tube containing the manganese oxide is heated to full redness and a rapid current of dry
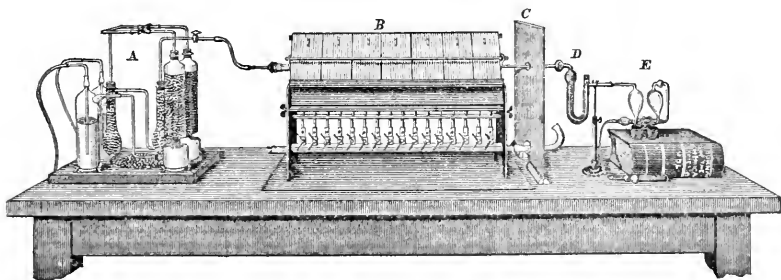
FIG. 3.

and pure air is passed through. The burners are shut off, except the last two or three, which are sufficient to keep about two inches of the tube red hot. The current of air is then stopped and the calcium chloride tube and potash bulbs are attached, and finally the substance is introduced in a platinum or porcelain boat (by

[1] A porcelain boat is preferred in most cases, as the substance burns more uniformly in it than in a platinum boat.

removing the coupling at the posterior end) followed by the roll of platinum gauze. A slow current of air is then turned on, it having been purified by passing through the apparatus shown at *A*, Fig. 3, containing, 1st, a strong solution of caustic potash; 2d, pumice and sulphuric acid, and, 3d, solid caustic potash. Two burners under the portion of the tube containing the roll of platinum gauze are now lighted, and the substance is gradually approached by lighting the burners under the manganese oxide. The red-hot platinum gauze will decompose any condensable gases which may diffuse back, if the combustion should proceed a little too rapidly, and prevent a deposit in the posterior portion of the tube outside of the furnace. An asbestos shield *C*, Fig. 3, protects the calcium chloride tube and potash bulbs from the heat of the furnace.

I prefer to use a Geissler potash bulb with tube for solid potash attached, in which case the air or oxygen may be forced in at the rate of two or three bubbles a second. It is also desirable to use a slight exhaust as well as pressure.

When all of the burners have been lighted, the air is replaced by a current of oxygen, which is continued for about fifteen minutes, when the combustion will have been completed. The burners are then all turned off excepting the three at the end under the manganese oxide, and the bulbs are disconnected and set aside to cool. In a few minutes the platinum gauze may best be removed with a bent wire, and if a second set of bulbs be ready, another combustion may proceed at once. In this way a combustion may be made easily every hour, the actual time consumed in burning the substance being from thirty to forty minutes.

The manganese oxide is regenerated by the oxygen which is passed in during each combustion; it is never reduced below MnO and therefore can do the platinum tube no damage. We have a platinum tube in which over fifty combustions were made during two months without removing the manganese oxide, and on examination afterward, the inside of the tube was found to be as clean and sound as ever.

As for the accuracy of the method, I will simply give five results of the analyses of sugar made by Mr. L. M. Donaldson under my direction:

No.	Carbon.	Hydrogen.
I.	42.00	6.62
2.	42.20	6.52
3.	42.02	6.56
4.	42.08	6.55
5.	42.07	6.24
Mean,	42.07	6.49
Theory,	42.10	6 44
Error,	—.03	+.05

I also give five results obtained by him by the same method, using a glass tube instead of platinum. They are as follows:

No.	Carbon.	Hydrogen.
I.	41.90	6.43
2.	41.92	6.37
3.	42.05	6.41
4.	42.24	6.36
5.	41.99	6.37
Mean,	42.02	6.39
Theory,	42.10	6.44
Error,	— .08	— .05

The method of carrying on the combustion of liquids of high boiling point is similar to that for solids. The required amount of liquid is placed in the boat and the combustion proceeded with as before, except in most cases it is best to approach the substance with the heat a trifle more slowly. For convenience in weighing and handling such liquids, I have used the arrangement shown in Fig. 4. It consists simply of a thin glass bottle with a stopper B, through which passes a tube C, reaching to the bottom. A is rubber bulb attached to the end of the tube, forming an ordinary liquid dropper. The bottle

Fig. 4. containing the liquid is weighed, and after the requisite amount of the substance for combustion has been transferred to the boat by means of the dropper, the whole is weighed again.

In the case of very volatile liquids, the following method is employed: The volatile liquid is drawn into the bulb A, about 3.5 cm. in diameter, shown in Fig. 5, and the whole weighed. The bulb is then connected by the limb D to the combustion tube, and by the other to the purifying apparatus A, Fig. 3. The combustion tube is filled three-fourths full of manganese oxide, and

heated to redness before the bulb containing the liquid is attached ; the calcium chloride and potash bulbs are also previously connected. A slow current of nitrogen is then passed through the apparatus to serve simply as a carrier of the vapor of the substance, and to avoid danger of explosion, which would exist if oxygen or air was employed for the same purpose. A few inches below the bulb *A*, Fig. 5, is placed an iron plate *B*, of sufficient size to evenly

FIG. 5.

distribute the heat, which is furnished by the lamp *C*, through the bulb and connecting tubes, so as to prevent the condensation of the liquid *en route* to the combustion tube. The temperature of the plate should be so regulated as to rapidly evaporate the liquid in the
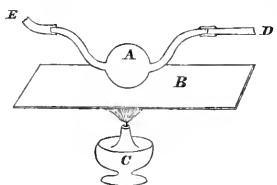
bulb, but without boiling it. After all of the liquid has left the bulb and passed into the combustion tube, the current of nitrogen is cut off, and air or oxygen is turned on. The latter is always preferred. The use of nitrogen in no way interferes with the combustion of the substance, and the absorption of it by the potash bulb is not materially appreciable in the results. The nitrogen may be prepared sufficiently pure by passing air over red hot copper in a porcelain tube, and then through caustic potash to a gas-holder.

As mentioned before, a glass combustion tube may be used, in which case, of course, it should be straight, with stoppers fitting at each end. When glass is employed, a little more time is necessarily required, owing to the caution which must be used in heating and cooling.

I do not deem it necessary to speak of the advantages of the platinum over the glass tube, but I will simply say that its cost is soon paid for in time and labor saved.

I prefer manganese oxide to copper oxide, even if the old method of combustion is employed, because it is much lighter, quite as effective, and forms a mass more easily permeable by the gases.

ON THE OCCURRENCE OF SOLID HYDROCARBONS IN PLANTS.

By Helen C. De S. Abbott and Henry Trimble.

When many plants of the higher botanical orders are exhausted with petroleum-ether, crystalline compounds may be separated from the extracts which have not been previously noticed. The compounds are also obtained when alcohol or ether is used as a solvent; but it is preferable, on account of the greater number of constituents extracted by these menstrua, to employ petroleum-ether, and thus avoid certain difficulties of separation. Among the plants in which to this time these compounds have been discovered, may be mentioned *Cascara amarga*, *Phlox Carolina* and the *Phlox* species, and in other species of three or four natural orders.

The crystals from these petroleum-ether extracts were first noticed in 1884 and were announced in 1886 as a "camphor-like body."

Subsequent investigations proved this body to be a mixture; and by extracting 25 and 20 kilos of *Cascara amarga* and *Phlox Carolina* respectively, a satisfactory quantity was obtained. The method adopted to purify was, after removal of fats and coloring matter, to crystallise from boiling absolute alcohol. By fractional crystallisation at least three different compounds have been separated. One only of these has been studied. It melted at 196.2° C. to 196.4° C.; at higher temperatures it was decomposed, with an odor like sandal wood. It was soluble in petroleum-ether, ethylic and acetic ethers, benzol, chloroform, hot alcohol, glacial acetic acid, acetic anhydride, and linseed oil. From most of these solvents it readily separated in silky acicular crystals, often two to four centimeters in length.

The first ultimate analysis of this purified product from *Cascara amarga* gave the following results:

	I.	II.	III.
C	86.30	86.29	86.33
H	12.96	12.96	12.83
	99.26	99.25	99.16

These figures pointed strongly to the conclusion that the compound was a solid hydrocarbon. Liquid hydrocarbons are abundant in the plant kingdom, but a similar occurrence of this class of compounds in a solid or crystalline condition appears not to have been noticed.

By further purification of an additional quantity of the mixture the following results were obtained:

I. 0.1058 gram gave 0.3413 CO_2 and 0.1133 H_2O.

II. 0.1113 gram gave 0.3588 CO_2 and 0.1193 H_2O.

	I.	II.
C	87.97	87.89
H	11.89	11.90
	99.86	99.79

Fifteen kilos of *Phlox Carolina* were exhausted, the compound separated and repeatedly crystallised. Its ultimate analysis gave the following:

I. 0.1117 gram gave 0.3600 CO_2 and 0.1208 H_2O.

II. 0.1314 gram gave 0.4228 CO_2 and 0.1421 H_2O.

	I.	II.	Theory for $(C_{11}H_{18})_x$.
C	87.90	87.76	88.00
H	12.02	12.02	12.00
	99.92	99.78	100.00

ON THE RELATIONS EXISTING BETWEEN CARBAZOL AND PYRROL.

By Samuel C. Hooker.

The theoretical relation existing between carbazol, indol, and pyrrol is well shown by comparing their formulæ as follows:

Carbazol.   Pyrrol.   Indol.
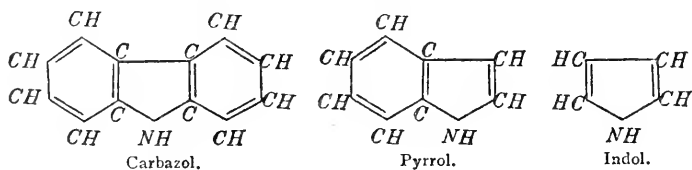
The analogy existing between indol and pyrrol has received important experimental demonstration from the researches of v. Baeyer, E. Fischer,[1] and Ciamician,[2] but up to the present time no material evidence has been accumulated to show that a similar relation exists between carbazol and pyrrol. The formation of carbazol from thiodiphenylamine[3] by the action of copper furnishes some proof in support of the formula given above; but as this is the only reaction clearly tending to show that carbazol is a di-ortho derivative of diphenyl, and therefore that it contains the pyrrol ring, further evidence in the same direction appears desirable.

In making the experiments which led up to the facts here recorded, I hoped to find points of resemblance between carbazol and pyrrol for which the $>$NH group alone, independent of the pyrrol ring, would not account, and thus to confirm indirectly the above formula of carbazol.

Runge, the discoverer of pyrrol, observed that its vapor in contact with pine moistened with hydrochloric acid, colored the wood intensely red. Von Baeyer subsequently described this reaction as being very characteristic of indol. It is interesting, therefore, to find that carbazol reacts similarly, though not so readily. In order to observe the reaction, soak the wood—an ordinary match-stem answers admirably—for a second or two in a hot alcoholic or acetic acid solution of carbazol, and then thrust it into the neck of a bottle containing concentrated hydrochloric acid, so as thoroughly to expose it to the action of the gas without bringing it in contact with the acid solution. The red color soon develops, and slowly increases in intensity. The shade is precisely similar to that produced by pyrrol.

Since carbazol may be regarded as a derivative of indol in which the two carbon atoms of the indol ring are connected with the group C_4H_4'', this observation appears directly to contradict one of the deductions made by Emil Fischer[4] in the course of his study of indol derivatives. "The fir-wood reaction," he says, "no longer occurs when both the carbon atoms of the indol ring are connected with alkyls."

It seemed necessary, therefore, to confirm my results by substituting synthetical carbazol for that extracted from coal tar, with which I first obtained the reaction. In spite of careful purification,

[1] Ber. d. chem. Ges. **19**, 2988.   [2] Ibid. **19**, 3028.   [3] Ibid. **20**, 232.   [4] Ibid. **19**, 1570.

it is conceivable that the coal-tar carbazol might still retain traces of foreign substances capable of imparting to it the power of coloring the wood.

Through the kindness of Dr. A. Goske in forwarding to me a sample of carbazol recently obtained by him[1] by the action of copper on thio-diphenylamine, I have been able to confirm the results of previous experiments in a satisfactory manner.

It seems possible therefore that the di-alkyl derivatives of indol which do not, according to Emil Fischer, give the fir-wood reaction when the test is made in the usual way, may do so if the conditions of the experiment are somewhat varied.

Carbazol and Isatin.

The behavior of thiophene (and furfuran) in forming coloring matters with isatin and ortho-diketones, apparently similar to those of pyrrol, makes it probable that in such reactions the $>$NH group of pyrrol takes no part. Consequently, in the case of carbazol, as all the hydrogen atoms of the pyrrol ring, excepting that of the imide group, are already substituted, it is not to be expected that any similar coloring matters can be formed. For this reason I was surprised to find that the behavior of carbazol and isatin in the presence of sulphuric acid is such as to strongly suggest the indophenine reaction.

On adding concentrated sulphuric acid to carbazol and isatin, an intense blue color is developed as the substances dissolve. The reaction is extremely characteristic and can be used as a delicate test for the recognition of carbazol. The blue color of the solution does not appear to be affected by slightly warming, and even after standing some hours its intensity had not materially diminished or its color otherwise changed. Water precipitates an indigo-blue substance which very rapidly becomes lighter in color. In order to avoid this change, attempts were made to extract the blue coloring matter from the acid solution without the addition of water, by agitation with various solvents. These experiments proved unsuccessful, and the further study of the compound was abandoned.

Although the above is very like the indophenine reaction and its apparently analogous reaction in the case of pyrrol, I am inclined to believe, for considerations already mentioned, that the similarity

[1] Ber. d. chem. Ges. **20**, 232.

is apparent only and not real. Diphenylamine gives no reaction with isatin under the same circumstances.

Since diphenylene-oxide and diphenylene-sulphide are probably related to furfuran and thiophene, respectively, in the same way as carbazol is to pyrrol, it seemed of importance to ascertain whether these substances also behaved similarly with isatin. I was unable to obtain any reaction with diphenylene-oxide, and consequently it is probable that diphenylene-sulphide also will be found indifferent.

Carbazol and Quinone.

The compounds produced from pyrrol and benzoquinone have no corresponding members in the thiophene series, and would appear to be directly or indirectly dependent upon the $>$NH group for their existence ; it therefore seemed possible that carbazol and benzoquinone might react with the formation of similar compounds.

If a small quantity of sulphuric acid, diluted with one or two volumes of acetic acid, is added drop by drop to an acetic acid solution of carbazol and benzoquinone, an intense carmine red solution is produced which passes into a reddish violet as the quantity of sulphuric acid is increased. Water precipitates from this solution a substance of the same color, which dissolves very readily in ether, chloroform, and alcohol.

On the addition of crystals of quinone to carbazol dissolved in concentrated sulphuric acid, an intense green color is imparted to the solution. Hence, according to the strength of the acid used, a reddish-violet or a green solution is obtained.

Similarly Victor Meyer and O. Stadler[1] have shown that benzoquinone reacts with pyrrol in two distinct ways. If aqueous solutions of the two are mixed, a violet coloring matter is produced, whereas in the presence of dilute sulphuric acid a green precipitate is formed. For purposes of comparison I repeated V. Meyer and Stadler's experiments. The violet coloring matter obtained dissolved in ether to a solution very similar in shade to that of the ethereal solution of the coloring matter from carbazol.

Before concluding that the formation of these compounds is in any way connected with the existence of the pyrrol ring, it seemed necessary to study the action of diphenylamine under similar

[1] Ber. d. chem. Ges. **17**, 1035.

circumstances. Sulphuric acid added to diphenylamine and quinone dissolved in acetic acid immediately colors the solution blue ; on adding water, a violet substance is precipitated.

These reactions recall the coloring matters obtained by P. Greiff[1] by heating chloranil or quinone with methyldiphenylamine and other amines with or without the addition of zinc chloride. The similarity existing between the method of formation and the shade of Greiff's coloring matters and the violet compounds obtained as above described from pyrrol, carbazol and diphenylamine, renders it extremely probable that in both cases the coloring matters are perfectly analogous, and that their formation in the case of pyrrol and carbazol depends upon the amine character of these substances, and not upon the presence of the pyrrol ring. This view, which could not, unfortunately, be substantiated by analysis, owing to the great instability of the pyrrol compound, receives support from the fact already alluded to that thiophene gives no coloring matters with benzoquinone.

With reference to the green solution formed on adding quinone to carbazol dissolved in sulphuric acid, it seems probable that in this case quinone plays the part of an oxidising agent only, for the same green-colored solution is produced, as is well known, by the addition of oxidising agents generally under similar circumstances. It occurred to me therefore as not unlikely that quinone acts· merely as an oxidising agent also, when in contact with pyrrol in acid solution, especially as V. Meyer and Stadler extracted hydroquinone in considerable quantities from the mother-liquor after the green compound had been filtered off. Confirmation of this view was obtained by reference to Anderson's[2] description of the properties of pyrrol. He states that ferric chloride causes a dilute hydrochloric acid solution of pyrrol to turn first *green* and then black. He adds that platinic chloride and potassic bichromate produce a black precipitate with the same solution.

A few experiments soon proved that not only ferric chloride, but potassic chromate or bichromate, platinic chloride, potassic ferricyanide, and even potassic nitrite under certain circumstances, all give, when added in small quantity to a dilute sulphuric acid solution of pyrrol, a green substance which passes more or less rapidly, according to the oxidising agent used and the acidity and degrees of concentration of the solutions employed, into the black

[1] Ber. d. chem. Ges. **12**, 1610.   [2] Ann. Chem. (Liebig), **105**, 354.

compound observed by Anderson. With tolerably concentrated solutions of the oxidising agents, the transition is so rapid that the green color can be scarcely observed, even when the sharpest lookout for it is maintained throughout the experiment.

With a dilute solution of potassic chromate, the formation of the green substance may be readily seen, and the reaction compared with that of quinone. As it is not easy, however, to obtain the reaction at its best without a number of trials, I prefer to give the exact strength of the solutions which I found to give good results. Eight drops of pyrrol are dissolved in 10 cc. of water to which eight drops of sulphuric acid have been added. When this is mixed with an 0.1 per cent. solution of potassic chromate in equal volumes, the green color is almost immediately developed, and rapidly increases in intensity until the solution becomes perfectly opaque. At this stage three or four volumes of water are added. The diluted solution is green in color, and slowly deposits a dark green or black precipitate.

A very dilute aqueous solution of quinone behaves almost precisely similarly with the above solution of pyrrol, but the precipitate formed is at first much greener than when potassic chromate is the oxidising agent used. It gradually darkens, however, and after some hours becomes almost black. If the green precipitate from quinone is washed with an 0.05 per cent. solution of potassic chromate, it is very rapidly blackened.

From these experiments it would appear extremely probable, therefore, that quinone does not condense with pyrrol in acid solution, but merely acts like other oxidising agents.

The formation of green substances like the above is not confined to the action of oxidising agents on carbazol and pyrrol. It has long been known that nitrous acid and other oxidising agents added in small quantity to diphenylamine dissolved in sulphuric acid, produce an intense blue solution from which water precipitates a green compound ; this, like the corresponding compounds from carbazol and pyrrol, is insoluble in ether.

Pyrrol and Picric Acid.

The behavior of indol and carbazol in combining with picric acid suggested the idea that probably pyrrol would form a similar compound. On adding picric acid to an excess of pyrrol, a red color is at once developed ; on warming, the picric acid is dissolved, and

the solution, when cold, deposits beautiful red needles. Similarly, if picric acid and an excess of pyrrol are dissolved in alcohol, long red needles, half or three quarters of an inch in length, can be readily obtained as the solution is allowed to evaporate. The compound is very unstable, and commences to decompose in the air as soon as the crystals are dry. Its fusing point is about 71°. Since the basic properties of pyrrol are very weak, and no well defined salts have been obtained with acids generally, the above described compound must be considered as analogous to the picric acid compounds of the hydrocarbons. The relation of pyrrol to benzol, so often dwelt upon by Victor Meyer, is thus once again emphasised. Phenyl-pyrrol also forms an unstable compound with picric acid. The compounds of pyrrol and its derivatives with picric acid will be further studied, and an attempt will be made to analyse them.

ON THE ACTION OF ETHYLENE BROMIDE ON THE SODIUM DERIVATIVES OF THE ETHERS OF ACETO–ACETIC, BENZOYL–ACETIC AND ACETONE–DICARBOXYLIC ACIDS.

BY P. C. FREER AND W. H. PERKIN, JR.[1]

The remarkable difference in the behavior towards tri-methylene bromide of the sodium derivative of malonic ether as compared with those of aceto-acetic, benzoyl-acetic, and acetone-dicarboxylic acids has previously been shown by one of us.[2] In the case of malonic ether, a tetra-methylene derivative, the so-called tetra-methylene-dicarboxylic ether,

$$(COOC_2H_5)_2 \; C\text{——}CH_2$$
$$\vert \qquad \vert$$
$$CH_2\text{—}CH_2$$

was formed; whereas, for example, by substituting ethylic sod-aceto-

[1] Abstract of a paper which appeared in the Journal of the Chemical Society (London), Vol. 51, p. 820. Communicated by the authors.

[2] W. H. Perkins, Jr., J. Chem. Soc. **51**, 702.

acetate, no tetra-methylene derivative was produced, a reaction which is represented by the following equation taking place:

$$2 \genfrac{}{}{0pt}{}{CH_3 - CO}{COOC_2H_5} {>} CHNa + BrCH_2 - CH_2 - CH_2Br =$$

$$\genfrac{}{}{0pt}{}{CH_3 - C \underline{\quad} O}{\underset{COOC_2H_5\ C - CH_2 - CH_2}{\overset{||}{}}} {>} CH_2 + \genfrac{}{}{0pt}{}{CH_3 - CO}{COOC_2H_5} {>} CH_2 + 2NaBr,$$
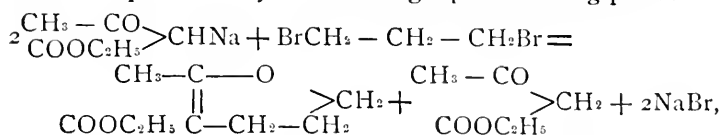
a body which has been called methyl-dehydro-hexone-carboxylic ether being formed.[1]

In a paper published some time ago, the results of a series of experiments on the action of ethylene bromide on sodium aceto-acetic and sodium benzoyl-acetic ethers were given. The substances formed in this reaction were assumed to be tri-methylene derivatives. Thus the reaction between sodium aceto-acetic ether and ethylene bromide was represented as taking place according to the following equation:

$$2 \genfrac{}{}{0pt}{}{CH_3 - CO}{COOC_2H_5} {>} CHNa + BrCH_2 - CH_2Br =$$

$$\genfrac{}{}{0pt}{}{CH_3 - CO}{COOC_2H_5} {>} C \genfrac{}{}{0pt}{}{CH_2}{CH_2} + \genfrac{}{}{0pt}{}{CH_3 - CO}{COOC_2H_5} {>} CH_2 + 2NaBr.$$
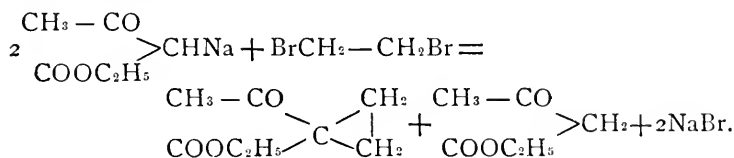
From the results of the experiments with tri-methylene bromide, mentioned above, it seemed, however, more probable that the above decomposition would be represented as follows:

$$2 \genfrac{}{}{0pt}{}{CH_3 - CO}{COOC_2H_5} {>} CHNa + BrCH_2 - CH_2Br =$$

$$\genfrac{}{}{0pt}{}{CH_3 - C - O}{\underset{COOC_2H_5C - CH_2}{\overset{||}{}}} {>} CH_2 + \genfrac{}{}{0pt}{}{CH_3 - CO}{COOC_2H_5} {>} CH_2 + 2NaBr,$$
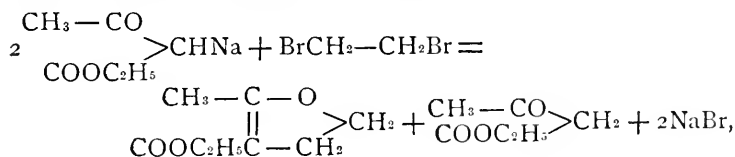
[1] After some discussion, we have decided upon the following system of nomenclature for this and similar bodies having a carbon-oxygen ring:

$$\begin{array}{ccc} CH_2 - CH_2 & CH_2 - CH_2 & CH_2 \\ | \quad\quad | & | \quad\quad | & \wedge \\ CH_2 - O & CH_2 \quad CH_2 & H_2C \quad CH_2 \\ \text{Tetrone.} & \vee & | \quad\quad | \\ & O & H_2C \quad CH_2 \\ & \text{Pentone.} & \vee \\ & & O \\ & & \text{Hexone.} \end{array}$$
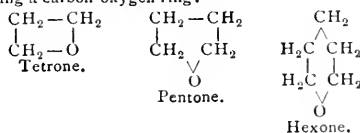
A body of the formula $\genfrac{}{}{0pt}{}{CH_3 - C \overset{\overset{O}{\wedge}}{} CH_2}{\underset{CH_2}{COOC_2H_5C \underset{||}{} \underset{\vee}{CH_2}}}$ is therefore methyl-dehydro-hexone-carboxylic ether.

in which case the product would be ethylic methyl-dehydro-pentone carboxylate. This possibility made it necessary to study the reaction again in the hope of being able to determine whether these compounds were pentone or tri-methylene derivatives. In experimenting with this end in view, a large number of reactions have been studied, the majority of which can be equally well explained on the assumption of either the tri-methylene or the pentone formula, the only one which has thrown any decisive light on the question being that which takes place when the acid which has already been described as acetyl-tri-methylene-carboxylic acid is distilled.[1] The acid is, during this operation, split into carbonic anhydride and a colorless oil which proved to be a mixture of two substances, the one which is present in by far the larger quantity being the substance which was previously (loc. cit. p. 710) described as acetyl-tri-methylene, boiling at 113°; the other, and lesser in quantity, being an oil of ethereal odor, boiling at 90°. The constitutional formulæ of these two substances, the latter having proved to be the anhydride of aceto-propyl alcohol, are therefore :

$$CH_3COC{<}{\overset{CH_2}{\underset{CH_2}{|}}} \qquad \overset{CH_3C{-\!-}O}{\underset{CH-CH_2}{\overset{||}{}}}{>}CH_2$$

Acetyl-tri-methylene,   Methyl-dehydro-pentone,
b. p. 113°.   b. p. 93° (?).
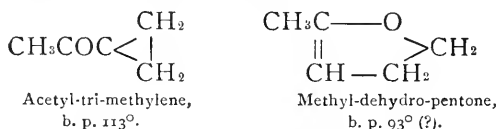
The remarkable difference between these two compounds is seen in their behavior towards water at ordinary temperatures. Acetyl-tri-methylene does not dissolve, and remains unchanged, whereas methyl-dehydro-pentone is converted into aceto-propyl alcohol.

$$\overset{CH_3-C{-\!-}O}{\underset{CH-CH_2}{\overset{||}{}}}{>}CH_2 + H_2O = \qquad \overset{CH_3-CO}{\underset{CH_2-CH_2-CH_2OH.}{|}}$$

Methyl-dehydro-pentone.   Aceto-propyl alcohol.
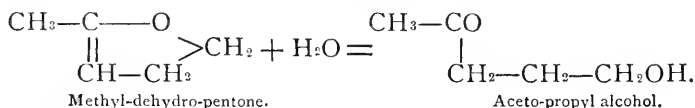
The latter is soluble in water.

The further examination of acetyl-tri-methylene has shown that it is a methyl-ketone, and a saturated body, so that the only formula which can be assigned to it, at all events according to our present knowledge of chemical structure, is the one given above.

The constitution of ethylic acetyl-tri-methylene carboxylate, as deduced from the above experiments, is very remarkably supported by the study of its magnetic rotation, as well as that of its

[1] J. Chem. Soc. **47**, 702.

decomposition products, which has been undertaken by W. H. Perkin, Sr. The only constitutional formula possible for ethylic acetyl-tri-methylene carboxylate other than that given above, is that of ethylic vinyl-aceto-acetate,

$$CH_3—CO$$
$$\quad\quad\quad | $$
$$COOC_2H_5CH—CH:CH_2$$
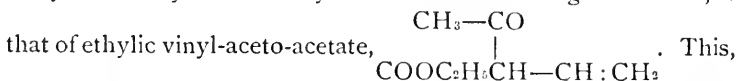
. This, however, differs from allyl-aceto-acetic ether in having one CH_2 group less than the latter. It therefore follows that the magnetic rotation of vinyl-aceto-acetic ether should be that of allyl-aceto-acetic ether (10.383) less the value of one CH_2 group (1.023), that is, it should be 9.360. Now, the magnetic rotation of the purest sample of acetyl-tri-methylene-carboxylic ether as yet examined is 8.198, a number which shows that it cannot be vinyl-aceto-acetic ether.

Against the conclusions deduced from the results of the chemical examination of the products of distillation of acetyl-tri-methylene-carboxylic acid it might be urged that during this reaction some intra-molecular change had taken place. The following considerations will show that this is not the case. The magnetic rotation of acetyl-tri-methylene is 5.245. If acetyl-tri-methylene is really the basis of the original product of the action of ethylene bromide on sodium aceto-acetic ether, it follows that the magnetic rotation of this substance should differ from that of acetyl-tri-methylene-carboxylic acid by the value of the group ($COOC_2H_5$—H). This number is easily obtained by subtracting the magnetic rotation of acetone from that of aceto-acetic ether, and is thus found to be 2.987. If we now add this to the magnetic rotation of acetyl-tri-methylene we obtain the number 8.232 as the calculated magnetic rotation of acetyl-tri-methylene-carboxylic ether. This agrees closely with that actually found (8.198), so that at present both the chemical reactions and the physical measurements are in favor of the assumption that these compounds are tri-methylene derivatives.[1]

Of the samples used in determining the physical properties of acetyl-tri-methylene-carboxylic ether, some were prepared by careful fractioning of the raw product of the action of ethylene bromide on sodium aceto-acetic ether, while others were made by the action of ethyl iodide on the silver salt of acetyl-tri-methylene-carboxylic acid. The ether, as prepared by the latter method, is a colorless

[1] For a complete list of the numbers obtained as the magnetic molecular rotation of acid and alcohol ethers of the fatty series, as well as the methods employed in their determination, see W. H. Perkin, J. Chem. Soc. **45**, 421.

oil, boiling between 195.6 and 196.6, and giving as its magnetic molecular rotation the number 8.198.

In order to prepare acetyl-tri-methylene-carboxylic acid from its ethereal salt, the fraction of the crude product of the action of ethylene bromide on the sodium derivative of aceto-acetic ether, boiling between 180° and 200°, is mixed with twice the calculated quantity of caustic potash dissolved in methyl alcohol, and the whole then boiled for five hours on a water-bath. The alcohol is distilled off, the product dissolved in water, and the solution then evaporated in an open basin until the last traces of alcohol have disappeared; when cool, dilute sulphuric acid is added in excess, and the whole is then extracted about ten times with pure ether. The solution, upon evaporating, deposits the acid in the form of a slightly brownish oil.

Acetyl-tri-methylene-carboxylic acid, when boiled with water, is slowly converted into carbonic anhydride and aceto-propyl alcohol, thus:

$$CH_3 - CO \diagdown \quad \diagup CH_2 \qquad \qquad CH_3CO \qquad \qquad + CO_2.$$
$$\qquad \qquad C \quad | \quad + H_2O = \qquad | \qquad \qquad$$
$$COOC_2H_5 \diagup \quad \diagdown CH_2 \qquad \qquad H_2C - CH_2 = CH_2OH$$
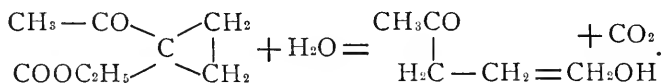
This reaction is complete at the expiration of fourteen hours, a clear solution resulting. Aceto-propyl alcohol is isolated from this by saturation with anhydrous potassic carbonate and repeated extraction with pure ether. After evaporating the ether, a colorless oil remains which cannot be purified by distillation at ordinary pressures, as it is decomposed, to some extent, into its anhydride and water. When rapidly fractioned under a pressure of 100 mm. it is obtained, nearly free from anhydride, as a colorless oil, boiling between 144° and 145°. Its magnetic rotation is 5.544; that of aceto-butyl alcohol, $CH_3.CO.CH_2.CH_2.CH_2.CH_2OH$, is 6.502; the difference between these two numbers being 0.958, a number closely agreeing with that of the true numerical value of the CH_2 group, viz. 1.023. This clearly shows that aceto-propyl alcohol and aceto-butyl alcohol must belong to a homologous series. The slight deviation is caused by the impossibility of obtaining aceto-propyl alcohol free from its anhydride. The constitution of aceto-butyl alcohol has been proved by the formation of acetic and succinic acids upon the oxidation of that substance with chromic acid. Aceto-propyl alcohol is a colorless syrup, mixing with water in all proportions. When slowly heated it is completely

decomposed into its anhydride and water, the distillate consisting of two layers which, however, form a homogeneous mixture after standing for some hours. The phenyl-hydrazine compound could not be obtained in a crystalline state.

As has been previously stated, acetyl-tri-methylene-carboxylic acid is decomposed, on distillation, into acetyl-tri-methylene and a volatile oil, boiling at 93°. This is identical with the anhydride of aceto-propyl alcohol. The difference between acetyl-tri-methylene and this anhydride has already been mentioned.

Ethylic acetyl-tri-methylene carboxylate combines readily with hydrogen bromide, ethylic ω-brom-ethyl aceto-acetate being formed, thus:

$$\begin{array}{c} CH_3 - CO \\ COOC_2H_5 \end{array}\!\!>\!\!C\!<\!\!\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array} + HBr = \begin{array}{c} CH_3CO \\ COOC_2H_5 \end{array}\!\!>\!\!C - CH_2 - CH_2Br.$$
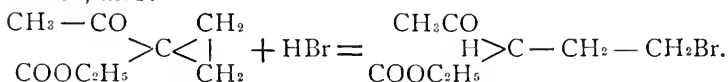
This is a heavy oil, of slightly yellowish color which changes to brown when the substance is exposed to the air, hydrogen bromide being at the same time evolved. The oil cannot be distilled. When treated with zinc dust and acetic acid, ethyl-aceto-acetic ether is produced. When boiled with dilute hydrochloric acid for about two hours, ethylic ω-brom-ethyl aceto-acetate is completely dissolved, carbon dioxide, alcohol, and aceto-propyl alcohol being produced. This latter was found to be identical with the alcohol as obtained by boiling acetyl-tri-methylene-carboxylic acid with water.

If aceto-propyl alcohol be dissolved in about five parts of water, and to this solution the theoretical quantity of three per cent. sodium amalgam be slowly added, reduction, without evolution of gas, sets in immediately. The product of this reaction is isolated by saturating the liquid with anhydrous potassic carbonate and extracting repeatedly with pure ether. By this means a colorless oil, boiling between 210° and 220°, with slight decomposition when rapidly distilled, is obtained. This substance is γ-pentylene-glycole,

$$\begin{array}{cc} CH_3.CH.CH_2.CH_2.CH_2 \\ OH \quad\quad\quad OH \end{array}.$$
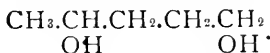
When this substance is heated on a water-bath with fifty per cent. sulphuric acid, it is decomposed into its anhydride and water. The latter is a volatile oil of ethereal odor, boiling between 78° and 83°. The formula of this substance is as follows:

$$CH_3 - CH.CH_2 - CH_2 - CH_2 - O$$
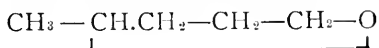
After the results obtained in studying the action of water on acetyl-tri-methylene-carboxylic acid, when, as has previously been stated, decomposition into carbonic anhydride and aceto-propyl alcohol takes place, it was thought that it would be interesting to experiment on the behavior of benzoyl-tri-methylene-carboxylic acid under similar conditions. One gram of the acid, in as finely divided a state as possible, was heated in a sealed tube with 40 cc. of water for four or five hours at 100°–110°, the tube being frequently taken out and well shaken. On opening the tube, the contents were found to consist of an almost perfectly clear liquid. In order to separate the few oily drops swimming about, the whole was filtered through a wet filter, and the product of the reaction separated from the now perfectly clear filtrate by saturation with anhydrous potassium carbonate and repeated extraction with ether. This ethereal solution, after drying, filtering, and evaporating, deposited a colorless oil of aromatic odor, which the analysis showed was not benzoyl-propyl alchohol, but the anhydride of that body. In this decomposition it is evident that the first reaction which takes place is the following :

$$\begin{matrix} C_6H_5-CO \\ \qquad \qquad >C< \\ COOH \end{matrix} \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} + H_2O = \begin{matrix} C_6H_5-CO \\ | \\ CH_2-CH_2-CH_2OH \end{matrix} + CO_2$$
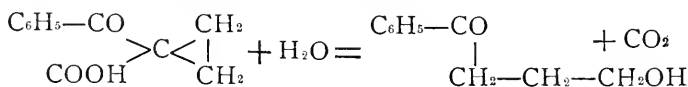
That a ketone alcohol is present in the aqueous solution can be proved by the addition of phenyl-hydrazine acetate, when an oily phenyl-hydrazine compound is at once precipitated. However, upon extracting with ether and drying over anhydrous potassic carbonate, this unstable ketone alcohol is at once converted into its anhydride and water :

$$\begin{matrix} C_6H_5-CO \\ | \\ CH_2-CH_2-CH_2OH \end{matrix} = \begin{matrix} C_6H_5-C-O \\ \qquad \quad || \qquad >CH_2 \\ CH_2.CH_2 \end{matrix} + H_2O.$$
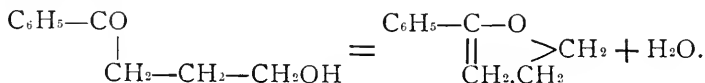
The instability of these aromatic ketone alcohols is very remarkable. Aceto-butyl alcohol, when rapidly heated, can be distilled almost without change, whereas the corresponding aromatic alcohol, benzoyl-butyl alcohol, is split into its anhydride and water on simply standing over sulphuric acid for a few days. Aceto-propyl alcohol, although not so stable as aceto-butyl alcohol, can be distilled unchanged under a pressure of 100 mm., whereas benzoyl-propyl alcohol only exists in aqueous solution, and on isolation

is at once converted into its anhydride. It still remains to be determined whether the anhydride of benzoyl-propyl alcohol is identical with the body previously described as benzoyl-tri-methylene.[1]

It seems almost probable that if these anhydride rings are so easily formed in the aromatic series, the derivatives obtained from benzoyl-acetic ether and ethylene bromide are to be classified as pentone and not tri-methylene substances, in which case the acid described as benzoyl-tri-methylene-carboxylic acid would have the formula,

$$C_6H_5 - C - O$$
$$\qquad\qquad \| \qquad >CH_2.$$
$$COOH - C - CH_2$$
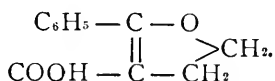
Further experiment must decide this point.

In order to prove the presence of a carbonyl group in acetyl-tri-methylene-carboxylic ether, several experiments on the action of phenyl-hydrazine on this substance were made. If the ether be mixed with a little less than the theoretical quantity of phenyl-hydrazine, the mixture then heated on a water-bath until all reaction has ceased, and the whole then submitted to distillation in steam, in order to drive off any unchanged ether, a heavy, brownish oil remains behind. This product, when allowed to stand for six weeks, gradually becomes crystalline. The analysis showed that one molecule of phenyl-hydrazine had reacted with one of the ether, so that the chemical change could be expressed as follows:

$$CH_3.CO.C.COOC_2H_5 + C_6H_5.NH.NH_2 =$$
$$\underset{CH_2 - CH_2}{\diagup\diagdown}$$

$$CH_3.C.C - COOC_2H_5 + H_2O$$
$$\underset{C_6H_5N_2HCH_2 - CH_2}{\Big|\;\Big|\diagdown}$$
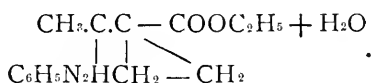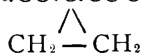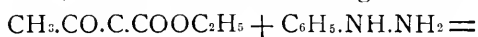
This would appear to be an additional proof that acetyl-tri-methylene-carboxylic ether is really a tri-methylene derivative, and does not contain an oxygen-carbon chain, as it would were its formula as follows:

$$CH_3 - C = C - COOC_2H_5$$
$$\qquad\quad | \qquad |$$
$$\qquad\quad O \qquad |$$
$$\qquad\quad | \qquad |$$
$$\qquad\quad CH_2.CH_2$$

During the course of these experiments it appeared interesting

[1] J. Chem. Soc. **17**, 840.

to try the action of oxidising agents on acetyl-tri-methylene-carboxylic acid, or its ethereal salt, in the hope that in this way tri-methylene-di-carboxylic acid (1.1) might be produced, thus:

$$CH_3 — CO — \underset{\underset{CH_2 — CH_2}{\diagup\!\diagdown}}{C} — COOH + 2O_2 =$$

$$COOH — \underset{\underset{CH_2 — CH_2}{\diagup\!\diagdown}}{C} — COOH + CO_2 + H_2O.$$

The experiments, both in acid solution with chromic acid, and in alkaline solution with potassic permanganate, as well as with iodine, gave negative results. As the chief products of oxidation, oxalic and acetic acids were observed, while in the case of iodine, iodoform was produced.

Phosphorus pentachloride reacts with acetyl-tri-methylene-carboxylic ether with great violence, the ether being dissolved in twice its volume of chloroform, and the calculated quantity of phosphorus pentachloride then added, the whole being kept cool by means of ice-water. The product is then poured into cold water, and the heavy oil which separates extracted with ether. By this means a heavy fluid is obtained, upon evaporation of the ether, the boiling point being between $171°$--$173°$, 150 mm. On each fractioning it was noticed that traces of hydrogen chloride were given off, so that, even under a pressure of 35 mm., some decomposition takes place upon boiling. This chlorinated compound is a colorless oil of powerful odor which, upon standing, soon becomes yellow. The analysis proved that it contained two chlorine atoms to the molecule. Its constitution can be expressed by either of the two following formulæ:

$$\overset{\text{I.}}{\underset{COOC_2H_5}{CH_3—CCl_2}} >C< \overset{CH_2}{\underset{CH_2}{\,|\,}} \qquad \overset{\text{II.}}{\underset{COOC_2H_5}{CH_3—CCl}} \diagdown\!\!\!\diagup\, C.CH_2 — CH_2Cl,$$

of which the second seems the more plausible. The most probable explanation of the action of phosphorous pentachloride on acetyl-tri-methylene-carboxylic ether is as follows: A substance, the constitution of which is represented by formula I, is first formed according to the equation:

$$\underset{COOC_2H_5}{CH_3 — CO} >C< \overset{CH_2}{\underset{CH_2}{\,|\,}} + PCl_5HCl = \underset{COOC_2H_5}{CH_3 — CCl_2} >C< \overset{CH_2}{\underset{CH_2}{\,|\,}} + POCl_3.$$

This substance is further acted upon by the hydrochloric acid which is always present; the tri-methylene ring is split, and a change takes place which can be represented by the following equation:

$$CH_3 - CCl_2 \diagdown C \diagdown \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} + HCl = \begin{matrix} CH_3 - CCl_2 \\ \\ COOC_2H_5 \end{matrix} \diagup CH - CH_2 - CH_2Cl.$$

This intermediate compound then loses one molecule of hydrochloric acid, probably during the reaction, possibly upon distillation, when a substance results, the constitution of which is represented by formula II:

$$\begin{matrix} CH_3 - CCl_2 \\ \\ COOC_2H_5 \end{matrix} \diagup CH - CH_2 - CH_2Cl =$$

$$\begin{matrix} CH_3 - CCl \\ \\ COOC_2H_5 \end{matrix} \diagup C - CH_2 - CH_2Cl + HCl.$$

The hydrochloric acid thus produced could react with a fresh quantity of the original compound, and thus a continuous reaction be set up. The behavior of this substance, which may be called ethylic chloro-ethyl-chloro-crotonate, toward reducing agents has tended to confirm the above speculations. By reduction with zinc dust and hydrochloric acid in alcoholic solution, an oil consisting of an acid and a neutral substance is obtained. These are separated by means of sodic carbonate, from which the acid is obtained as a crystalline solid when the solution is acidified. This crystalline body was found to correspond to chloro-ethyl-crotonic acid obtained by Demarcais by treating ethyl-aceto-acetic ether with phosphorus pentachloride. The formation of chloro-ethyl-crotonic acid from chloro-ethyl-chloro-crotonic ether can be explained according to the following formula:

$$\begin{matrix} CH_3 - CCl \diagdown \\ \\ COOC_2H_5 \diagup \end{matrix} C - CH_2 - CH_2Cl + H_2 =$$

$$\begin{matrix} CH_3 - CCl \diagdown \\ \\ COOH \diagup \end{matrix} C - CH_2 - CH_3 + C_2H_5Cl.$$
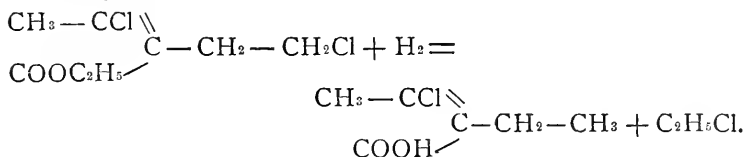
We intend repeating these experiments with larger quantities of substance. The neutral oil which was mentioned above has not been further examined.

By means of reduction of chloro-ethyl-chloro-crotonic ether with either sodium amalgam or hydriodic acid and phosphorus, di-ethyl-acetic acid was obtained, as follows:

$$CH_3CCl \atop COOC_2H_5 \Big\rangle C-CH_2-CH_2Cl+3H_2+H_2O =$$

$$CH_3CH_2 \diagdown \atop COOH \diagup HC-CH_2-CH_3+C_2H_5OH+2HCl.$$
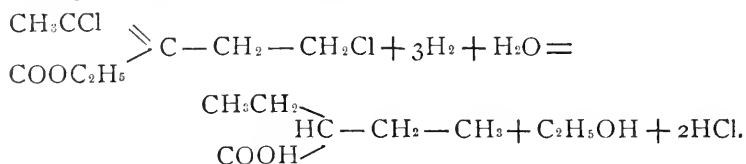
The action of ethylene bromide on acetone-dicarboxylic ether have some interesting results. In studying this reaction, a mixture of 40 grams of ethylic acetone-dicarboxylate and 38 grams of ethylene bromide was slowly added to a well cooled solution of 9 grams of sodium dissolved in 100 grams of alcohol and the whole boiled on a water-bath for ten hours. In order to isolate the principal product of the reaction, the excess of alcohol was distilled off, the residue mixed with water, and the whole extracted with ether. The yellowish oil which remained after evaporation of the ether was submitted to fractional distillation. It was found to consist for the most part of unchanged acetone-dicarboxylic ether and a colorless oil, boiling between 223° and 224° (150 mm.). The analyses of the latter agreed with the formula of ethylic acetyl-tri-methylene-dicarboxylate. This substance is quite unstable, a fact which accounts for the small yield, which was but ten per cent. Besides the oil boiling between 223° and 224°, another, boiling at 130°–200° (150 mm.), was separated. This latter, when refractioned at ordinary pressures, proved to be acetyl-tri-methylene-carboxylic ether.

Ethylic acetyl-tri-methylene carboxylate is produced from ethylic acetyl-tri-methylene dicarboxylate by partial hydrolysis and subsequent splitting off of carbon dioxide, thus:

$$COOC_2H_5-CH_2-CO \atop COOC_2H_5 \Big\rangle C\!\!<\!\!{CH_2 \atop CH_2}+H_2O =$$

$$COOH-CH_2-CO \atop COOC_2H_5 \Big\rangle C\!\!<\!\!{CH_2 \atop CH_2} = {CH_3-CO \atop COOC_2H_5} \Big\rangle C\!\!<\!\!{CH_2 \atop CH_2}+CO_2.$$
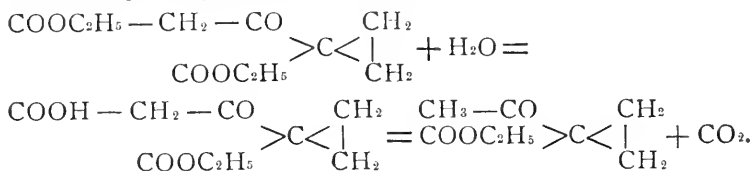
Acetyl-tri-methylene-dicarboxylic acid can only be prepared from its ethereal salt by saponification in the cold, twice the calculated quantity of pure potash dissolved in methyl alcohol being used. The reaction is complete at the expiration of twelve days. The

product is diluted with water, acidified with sulphuric acid, and extracted with ether. The crystalline acid is spread on a porous plate and washed with cold chloroform. Thus purified it is a white solid, melting with decomposition at about 175°. Upon boiling with water it is split into aceto-propyl alcohol and two molecules of carbonic anhydride, just as acetyl-tri-methylene-mono-carboxylic acid was decomposed into aceto-propyl alcohol and one molecule of carbon dioxide. When acetyl-tri-methylene-dicarboxylic acid is heated above its melting point, carbon dioxide is evolved and acetyl-tri-methylene formed.

These experiments with acetone-dicarboxylic ether were performed in the hope of obtaining a penta-methylene derivative, thus:

$$\begin{array}{ccc}
COOC_2H_5 - CHNa & BrCH_2 & \\
\qquad\qquad | & | & \\
\qquad\quad CO & + \quad | & = \\
\qquad\qquad | & | & \\
COOC_2H_5 - CHNa & BrCH_2 &
\end{array}$$

$$\begin{array}{c}
COOC_2H_5 - CH - CH_2 \\
\qquad\qquad | \qquad\quad | \qquad + 2NaBr. \\
\qquad\quad CO \qquad | \\
\qquad\qquad | \qquad\quad | \\
COOC_2H_5 - CH - CH_2
\end{array}$$
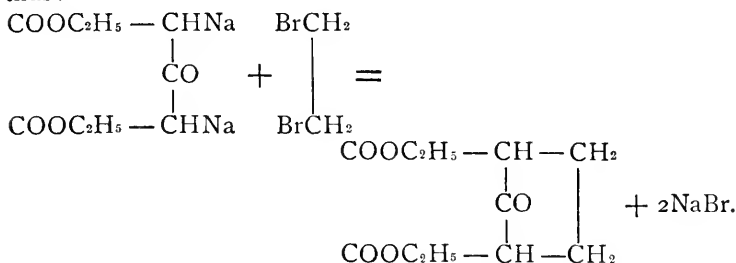
The result has shown that no such body is produced, the ether of acetyl-tri-methylene-dicarboxylic acid,

$$\begin{array}{c}
COOC_2H_5 - CH_2 - CO \qquad CH_2 \\
\qquad\qquad\qquad\qquad\qquad >C< \quad | \quad , \\
COOC_2H_5 \qquad CH_2
\end{array}$$
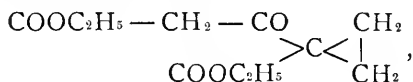
being formed.

Some of the reactions described in the foregoing, especially that of the decomposition of acetyl-tri-methylene-carboxylic acid upon boiling with water, are undoubtedly difficult to explain on the assumption that this substance, as well as the others mentioned, are really tri-methylene derivatives. At the same time it must be remembered that the properties of such a ring as that present in tri-methylene derivatives are at present wholly unknown, and that therefore no definite argument against their acceptance as such bodies can be based upon these peculiarities.

The foregoing research was conducted, in the beginning, in the laboratory of Prof. v. Baeyer, at Munich; later, at the kind invitation of Professor Dixon, we were enabled to continue it at the Owens College, Manchester, England.

COEFFICIENTS OF VOLATILITY FOR AQUEOUS CHLORHYDRIC ACID.

By Robt. B. Warder.

Aqueous chlorhydric acid may be represented by the formula $H_2O + nHCl$, where n is the number of molecules of the acid divided by the number of molecules of water. On boiling, the residue usually approaches the constant composition $H_2O + \frac{1}{8} HCl$, as shown by Roscoe and Dittmar. If the composition of the distillate formed at any moment is represented as $H_2O + vnHCl$, the factor v expresses the coefficient of volatility.

Chlorhydric acid of convenient strength was distilled, the boiling flask being so heated that no moisture should condense on the sides, to vitiate the results by dephlegmation. The several fractions of distillate were weighed and titrated, and the varying composition of the boiling liquid was calculated from the weights of water and acid removed.

In one distillation, with rapid boiling, the values agree well with the formula $v = 445n^3$, as shown by the following numbers :

n.	vn.		v.	
	Observed.	Calculated.	Observed.	Calculated.
.0681	.0095	.0095	.140	.140
.0759	.0147	.0148	.194	.195
.0862	.0243	.0245	.282	.285
.0984	.0422	.0417	.429	.424
.1107	.0661	.0669	.597	.604

The results obtained under the conditions of the experiments agree with the following statements, which must not be pressed too closely for other conditions :

I. When dilute acid ($n = .07$ to $.11$) was boiled rapidly, v was found to be equal to $445n^3$.

II. When dilute acid was boiled more slowly, the values of v were diminished about 10 to 30 per cent.

III. When strong acid ($n = .15$ to $.20$) was boiled rapidly, the values of v were greater than those indicated by the formula given above, being approximately represented by the equation $v = 3063n^4$.

Fuller details may be expected later.

THE ACTION OF SULPHURETTED HYDROGEN ON ARSENIC ACID.

(Sulphoxyarsenic Acid.)

By LeRoy W. McCay.

Introduction.

According to Wackenroder,[1] Ludwig[2] and H. Rose,[3] sulphuretted hydrogen first reduces arsenic acid to arsenious acid, with the separation of sulphur, and then precipitates the arsenic as the trisulphide. The reaction is said to take place in two distinct phases:

(1). $As_2O_5 + 2H_2S = As_2O_3 + 2H_2O + 2S$, and

(2). $As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$.
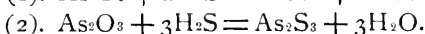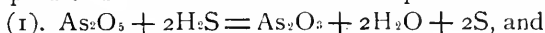
Fuchs[4] investigated the subject in 1862, and concluded that Rose and his predecessors were right. In 1878, Bunsen[5] proved that they were all wrong. He showed that when certain conditions were fulfilled, the arsenic present in an acidified solution of an arseniate could be directly and completely precipitated by sulphuretted hydrogen as the pentasulphide. Lately having had occasion to go over Bunsen's work, I[6] discovered that the arsenic in an acidified solution of an alkali arseniate could be directly and completely precipitated by sulphuretted hydrogen as the pentasulphide, in one hour, by simply causing the sulphuretted hydrogen to act upon the arsenic acid under pressure and in the absence of air.

Fresenius[7] says that when a current of sulphuretted hydrogen, in excess, is passed into an acidulated solution of arsenic acid, kept at 70° C., the pentasulphide is formed. The precipitate obtained under other circumstances, however, is, according to him, a mixture of the pentasulphide, trisulphide, and sulphur. Brauner and Tomiček[8] have of late done considerable work upon the subject. They substantiate Fresenius' results. With a hot solution of arsenic acid and a rapid current of sulphuretted hydrogen they obtained the pentasulphide; with a hot solution of arsenic acid and a slow current of the gas, they obtained a mixture of the pentasulphide, the trisulphide, and sulphur. They use the ordinary equations to indicate the reactions which take place during

[1] Dictate of Forensic Chemistry.
[2] Archiv der Pharm., 2te Reihe, **97**, 32.
[3] Ann. der Phys. u. Chem. **107**, 186.
[4] Ztschr. anal. Chem. **1**, 189.
[5] Ann. Chem. (Liebig) **192**, 305.
[6] This Journal **9**, 174.
[7] Qualitative Analyse, 15te Auflage.
[8] Chem. Soc. (Feb. 1888), 145.

the formation of the mixture. Why, when the current of gas is rapid, the pentasulphide is alone formed, while, when the current is slow, the mixture of the pentasulphide, the trisulphide, and sulphur results, they confess themselves unable to explain. They consider the problem as one belonging to the domain of chemical dynamics.

The object of this paper is to remove the mystery which is connected with the formation of the above-mentioned mixture of the pentasulphide, trisulphide, and sulphur. With the exception of that of Brauner and Tomiček, all the work which has thus far been undertaken with the view of explaining the irregularities connected with the action of sulphuretted hydrogen upon arsenic acid, has been of a qualitative nature. Bunsen's researches were essentially of an analytical character. In his paper upon the separation of antimony from arsenic with sulphuretted hydrogen, he did not endeavor theoretically to account for the fact that his precipitate, in determining the arsenic, was the pure pentasulphide and not the trisulphide and sulphur, or a mixture of the pentasulphide, the trisulphide, and sulphur.

The Reduction Hypothesis.

For some time past Rose's explanation has appeared to me inadequate. That it is partially false follows directly from the work of Bunsen, Fresenius, and Brauner and Tomiček. I believe that the experiments below described prove that reduction does not take place.

Having accidentally discovered that very small quantities of sulphuretted hydrogen produce, even after prolonged action, no precipitate of sulphide of arsenic in moderately concentrated solutions of alkali arseniates acidified with a mineral acid, I tried the following experiment :

25 cc. of a solution of potassium arseniate containing 25 grams of the salt in two liters of water were brought into a 200 cc. flask, and rendered faintly acid with sulphuric acid. 10 cc. of sulphuretted hydrogen water containing 0.0204 gram sulphuretted hydrogen were then added, and the whole was diluted with freshly boiled cold water to within about a centimeter of the mouth of the flask. The flask was then corked, well shaken, and allowed to stand in a cold place until all odor of sulphuretted hydrogen had disappeared, and a piece of paper moistened with acetate of lead and

held over the mouth of the flask gave no reaction for the gas. The flask and contents stood twelve hours.

At the end of this time a very slight opalescence appeared in the liquid, due to the separation of sulphur. In order to determine the weight of the sulphur, the contents of the flask were poured into a beaker containing some pure asbestus pulp, stirred thoroughly and filtered. The liquid passed through the filter perfectly clear. The pulp was thoroughly washed, dried over sulphuric acid, and then extracted with chemically pure carbon bisulphide. On evaporating the liquid, a slight residue of sulphur weighing 0.0005 gram was left. This corresponds to 0.00053 gram sulphuretted hydrogen.

The clear filtrate having been neutralised with sodium hydrate, mixed with sodium bicarbonate and a few drops of starch paste, was titrated with a $\frac{N}{10}$ solution of iodine. Instead of obtaining the elegant reaction so characteristic of Mohr's method for determining arsenious acid, I found it impossible to reach a point at which I could be sure that the reaction was complete. After 2–3 cc. of the iodine solution had been added, a bluish followed by a reddish color appeared, and this disappeared only after long and vigorous stirring. The phenomenon reminded me somewhat of the irregularities which, toward the end, invariably attend the titration with iodine of a solution of trisulphide of arsenic in sodium carbonate.[1] I have repeated this experiment several times, but the results have always been the same. It certainly disproves the reduction hypothesis; for if this hypothesis were true, the sulphur found, calculated to sulphuretted hydrogen, should have equalled 0.0204 gram, and the number of cubic centimeters of $\frac{N}{10}$ iodine used for titrating 10 cc. of the sulphuretted hydrogen water should have been equal to the number requisite for titrating the arsenious acid formed.

Sulphoxyarsenic Acid.

Since in all my experiments the quantity of sulphur formed proved so extremely small, it occurred to me that perhaps, by proper care, the separation of even traces might be prevented. Such, indeed, turned out to be the case. I found that by bringing 50 cc.

[1] Graeger. J. prakt. Chem. **96**, 261.

of the arseniate of potassium solution into a 500 cc. flask, acidifying
with 5 cc. dilute sulphuric acid (1 : 10), adding 10 cc. sulphuretted
hydrogen water, diluting to the mouth with freshly boiled cold
water, corking, shaking well, and keeping for twelve hours in a
dark place, and in a large vessel of ice-water, the solution lost
all smell of sulphuretted hydrogen and yet remained absolutely
clear.[1] The more dilute the solution and the lower the tempera-
ture, other things being equal, the less tendency there seems to be
toward a separation of sulphur. It is possible then, under certain
circumstances, for small quantities of sulphuretted hydrogen, in
the presence of relatively large quantities of arsenic acid, com-
pletely to disappear as such without either precipitating arsenic as
a sulphide or reducing arsenic acid to arsenious acid with the
separation of sulphur. This point having been settled, I turned
my attention to an examination of the liquid so obtained.

The first tests were performed upon a solution prepared pre-
cisely according to the details already given. Such a liquid, after
the removal, if necessary, of the trace of sulphur with asbestos
pulp, gave the following reactions : 1. When rendered strongly
acid with sulphuric or hydrochloric acid, it remained for some time
clear. 2. Mixed with sulphuretted hydrogen, it gave no precipitate.[2]
Sometimes hours passed before a precipitate commenced to
separate. 3. After boiling and shaking vigorously, it commenced
to become opalescent ; the opalescence gradually increased to a
cloud, and before long, sulphur was deposited. During the
reaction there was no sulphuretted hydrogen or sulphurous acid
generated. 4. After the boiled liquid had cooled and the sulphur
had been separated with asbestos, an addition of sulphuretted
hydrogen produced an instantaneous precipitate of trisulphide of
arsenic. 5. Sulphate of copper produced no precipitate. 6. Mer-
curic chloride gave a heavy yellowish white precipitate. 7. Nitrate
of silver produced immediately a heavy black precipitate of sul-
phide of silver. The filtrate from this contained no arsenious acid,
for, upon adding ammonia in excess, and a little more nitrate of
silver, and boiling, there was no reduction to metallic silver.

[1] To 500 cc. water I added 0.25 cc. sulphuretted hydrogen water, and then a few drops of
iodine solution. After standing about an hour, the liquid became distinctly opalescent. The
0.25 cc. sulphuretted hydrogen water = 0.0003 gram sulphuretted hydrogen.

[2] When there had been no separation of sulphur, the sulphuretted hydrogen produced
absolutely no color. When sulphur had separated, the liquid, after the addition of the sulphu-
retted hydrogen, took on a faint yellow hue.

The liquid being clear, acid, and absolutely free from uncombined sulphuretted hydrogen, could contain no soluble sulphides, no sulpho-salts, and no hyposulphites. These compounds cannot exist, much less be formed, in the presence of strong mineral acids. Such being the case, it seemed possible that the compound which gives the above reactions might be one intermediate between arsenic and sulpharsenic acid, or sulphoxyarsenic acid.[1]

By passing a current of sulphuretted hydrogen slowly through a cold acidified solution of potassium arseniate until an opalescence appeared, removing the excess of gas with a few drops of sulphate of copper, and filtering, a liquid was obtained which gave all the above reactions. The reactions, however, were not as definite as could be desired. To render them so, I heated the solution of arsenic acid to about 70° C., treated it with a slow current of sulphuretted hydrogen until a yellow precipitate made its appearance, and then suddenly poured the whole upon crushed ice. After stirring well, decanting, and removing the free sulphuretted hydrogen by means of a few drops of sulphate of copper and filtering, I obtained a liquid which gave six[2] of the seven reactions with a degree of sharpness leaving nothing to be desired. I also prepared a liquid which showed all the reactions, by heating the solution of arsenic acid to about 70° C., treating it with a slow current of gas until an opalescence appeared, cooling it suddenly by pouring it upon crushed ice, and removing the uncombined sulphuretted hydrogen by means of a blast of air.

Potassium Sulphoxyarseniate.

In 1845, Bouquet and Cloez[3] announced the discovery of a new and highly interesting salt, which they prepared by treating a saturated solution of biarseniate of potassium with a rapid current of sulphuretted hydrogen. The salt was carefully analysed and proved to be biarseniate of potassium, in which, according to the dualistic view, two atoms of the oxygen in the arsenic acid were replaced by an equivalent quantity of sulphur. They called the salt sulphoxyarseniate of potash, and wrote the formula for it, $As_2O_3.S_2,K_2O + 2H_2O$. Owing to the ease with which the solutions of the salt split up into arsenite of potassium, water and

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[1] See preliminary notice in the Chemical News **57**, 54.

[2] The presence of the sulphate of copper interferes with reaction No. 2.

[3] Ann. chim. phys., 3 Serie, **13**, 44.

sulphur, Bouquet and Cloez concluded that the corresponding acid could not exist in the free state. Since the paper of Bouquet and Cloez appeared, nothing has been published on the subject.[1] It appeared probable that the compound obtained by me might be the free sulphoxyarsenic acid.

In order to test this idea, the following experiments were made :

About half an ordinary test-tube full of a saturated solution of dihydrogen-potassium arseniate was treated for an hour with a rapid stream of sulphuretted hydrogen. The contents of the tube were then violently shaken for a few minutes, and permitted to stand until the precipitate formed had completely settled. Below the sulphide of arsenic there appeared a few colorless crystals. The mother-liquor, together with the sulphide of arsenic, were poured off as carefully as possible, the liquid immediately filtered, and, with it, the crystals were repeatedly washed until all yellow specks had been removed. The crystals were then washed with a very small quantity of pure water, pressed between filter paper, and dried over concentrated sulphuric acid in a vacuum. Only about 0.3 gram was obtained in this preliminary work, but the amount proved sufficient to substantiate my expectations and warrant further research.

To satisfy myself that I had to do with the pure salt, I made determinations of the arsenic and sulphur. The method of analysis in outline will be found further on.

Taken 0.2085 gram salt.

Calculated for $H_2KAsO_3.S$.		Found.
As	38.26	38.67
S	16.35	16.24

The figures found agree with those calculated, in a most satisfactory way, and there can be no doubt about the purity of the salt.

The rest of the crystals were dissolved in about 100 cc. of water, and the solution made acid with dilute sulphuric acid : 1. the liquid remained absolutely clear for some time ; 2. with sulphur-

[1] A. Geuther has described a sulphoxyarseniate of sodium, and K. Preis has lately prepared quite a number of what he calls oxysulpharseniates of sodium. These salts, however, were all obtained by acting on arsenious oxide with sulphide of sodium. Preis says that solutions of oxysulpharseniates of sodium, when boiled with excess of hydrochloric acid, give precipitates of pentasulphide of arsenic. Solutions of sulphoxyarsenic acid prepared as described in this paper give, when boiled with hydrochloric acid, a precipitate of sulphur. When the solutions are concentrated, this precipitate of sulphur is sometimes contaminated with traces of sulphide of arsenic. See A. Geuther, Ann. Chem. (Liebig) **240**, H. 2. Also K. Preis, Chem. Ztg. Repert. 1888, **23**, 73.

etted hydrogen it gave no precipitate ; 3. when boiled, decomposition set in and sulphur was deposited; 4. the boiled liquid gave with sulphuretted hydrogen an instantaneous precipitate of yellow trisulphide of arsenic ; 5. sulphate of copper occasioned no change ; 6. mercuric chloride produced immediately a yellowish white precipitate; 7. nitrate of silver threw down a heavy black precipitate of sulphide of silver. These are the reactions which characterised the liquid obtained by first passing a slow current of sulphuretted hydrogen through an acidified solution of an alkali arseniate, and then removing all traces of the free gas by means of copper solution or a blast of air.

The fact that a dilute solution of sulphoxyarseniate of potassium in water can be rendered strongly acid with sulphuric or hydrochloric acid, without any separation of sulphur, proves conclusively that sulphoxyarsenic acid can exist in the free state, and the reactions given by such a dilute solution of the acid being identical with those given by the liquid prepared according to any one of the above mentioned methods, likewise prove conclusively that the body with which we have to do, and which is the cause of all the mystery and irregularity connected with the precipitation of arsenic from a solution of arsenic acid with sulphuretted hydrogen, is sulphoxyarsenic acid.

The filtered mother-liquor obtained in preparing the sulphoxyarseniate of potassium gave excellent reactions for sulphoxyarsenic acid. This fact showed that large quantities of the salt had failed to crystallise out. The concentrated liquor, however, decomposed very rapidly, arsenite of potassium, water, and sulphur being formed. I found that this tendency to decompose could be in a great measure retarded by simply diluting the liquid with large quantities of water and keeping it cold.

I prepared two samples of sulphoxyarseniate of potassium for complete analysis. The method of preparation was essentially that of Bouquet and Cloez. The first sample was prepared by passing a rapid current of sulphuretted hydrogen through 250 cc. of a solution of dihydrogen-potassium arseniate, saturated in the cold, for about two hours. A little hydrate of potassium was added every now and then. The addition of this reagent seems to facilitate the separation of the salt, but it is not necessary, for the crystals obtained in the preliminary work separated out of the *strongly acid* solution of the potassium arseniate without any addition what-

ever of hydrate of potassium.   The mother-liquor and the sulphide of arsenic were poured off and filtered, and the crystals having been brought into a platinum dish, were repeatedly washed with portions of the filtrate from the sulphide of arsenic until all yellow specks had been removed.   The washing was continued with very small quantities of water, and ended with 90 per cent. alcohol and with ether.   This washing with alcohol and ether rendered the final drying and purification by pressing between folds of filter paper unnecessary.   The salt was allowed to remain in a vacuum and over concentrated sulphuric acid for several days, but this was really unnecessary, as I have since found that the salt after washing with alcohol and with ether is, after the ether has evaporated, perfectly dry.

The second sample was prepared in the same way, with the exception that the solution of dihydrogen-potassium arseniate, after the treatment with the gas, was allowed to stand over night in a cool place.   The crop of crystals thus obtained was larger than that resulting in the first case.   As Bouquet and Cloez, however, have already pointed out, the quantity of sulphoxyarseniate of potassium obtained is always extremely small in comparison with the quantity of arseniate of potassium used.   The sulphoxy-salt is somewhat more difficultly soluble in water than the ordinary arseniate, but the difference is not very marked, and therefore the quantity of the sulphoxy-salt which separates is necessarily small.

Analyses.

The salt in each case was oxidised with fuming nitric acid.   The moment the acid came in contact with the crystals, a cake of sulphur separated out, which was gradually oxidised to sulphuric acid.

The arsenic in I was determined as arseniate of silver;[1] the oxygen according to Bunsen's method; the potash as the double chloride of platinum and potassium; and the water, directly, by very carefully heating a portion of the sample in a glass tube in a current of dry air—the part of the tube directly in front of the boat containing the substance being plugged with a roll of strongly ignited copper gauze.

The arsenic in II was determined as the pentasulphide, according to my own method;[2] the oxygen was done by difference; and the potash and water exactly as in I.

[1] This Journal **8**, 77.   [2] Ibid. **9**, 174.

	Calculated for $H_2KAsO_3.S.$	I.	Found.[1] II.
As	38.27	38.29	38.36
S	16 35	15.60[2]	16.12
O	12.25	12.62	12.10
K_2O	23.98	23.91	23.96
H_2O	9.15	9.59	9.46
	100.00	100.01	100.00

A good deal of care must be taken in determining the water, owing to the fact that in heating the salt, a little arsenious acid is apt to sublime, and in spite of the copper gauze, pass partially into the chloride of calcium tube. I have found that by heating the solution of potassium arseniate saturated in the cold to boiling, removing the source of heat, and then treating the liquid with a rapid current of sulphuretted hydrogen until cold, the sulphoxyarseniate is formed more rapidly and in larger quantities. A considerable amount of sulphide of arsenic and sulphur separates out, but these can be easily removed by washing.

The reactions of a solution of potassium sulphoxyarseniate were compared very carefully with those of the liquid obtained by treating an acidified cold or warm solution of an alkali arseniate with a slow current of sulphuretted hydrogen, but no difference could be observed.

Sulphoxyarsenic acid and its salts can be distinguished from soluble sulphides by the fact that when mineral acids are added to dilute solutions, no sulphuretted hydrogen is evolved. The salts differ from sulpho-salts in that they are not precipitated in dilute solution by mineral acids. They cannot be mistaken for hyposulphites, for their solutions when heated with mineral acids give off no sulphur-dioxide, and their conduct toward silver solution is entirely different. Sulphoxyarsenic acid, it will be remembered, gives with silver solution instantaneously a jet-black precipitate of sulphide of silver, whereas in the case of a hyposulphite, the pre-

[1] Bouquet and Cloez found :

As	38.02
S	16.10
O	12.43
K_2O	23.69
H_2O	9.50
	99.74

For further information, see their memoir in the Annales de Chimie et de Physique, 3 Serie, **13.**

[2] Another determination gave 16.21 per cent. sulphur.

cipitate obtained with this reagent is first white, then yellow, next red, followed by brown, and finally black.

It should also be added that an ammoniacal solution of sulph-oxyarsenic acid gives with silver solution a black precipitate of sulphide of silver. This reaction will remind one of pentathionic acid, but pentathionic acid reduces indigo, and sulphoxyarsenic acid does not.

A solution of sulphoxyarseniate of potassium when rendered strongly ammoniacal gives no precipitate with magnesia mixture. This reaction will serve to distinguish sulphoxyarsenic acid from arsenic acid.

Rose's Experiment.

The mystery, then, which for so many years has been connected with the action of sulphuretted hydrogen on arsenic acid, here finds complete solution. The only wonder is that it has not been solved long ago. Rose undoubtedly had the sulphoxyarsenic acid in his hands when he was engaged in his study of the action of sulphuretted hydrogen on arsenic acid. He says distinctly that after treating the solution of arsenic acid for a short time with sulphuretted hydrogen, sulphur separates, which long remains suspended in the liquid. He says he had to let his liquid stand several days, and had to heat it repeatedly in order to collect the finely divided sulphur and render it possible to filter it off and get a clear filtrate. It seems to me hardly possible that after all this standing and heating, a solution which at first contained but a small amount of sulphuretted hydrogen could still retain enough of the gas to give with silver solution a black precipitate of sulphide of silver. And yet Rose, when he added silver solution to the filtrate from the sulphur, did get a black precipitate of sulphide of silver. In the light of the experiments described above, it appears highly probable that the black precipitate of sulphide of silver was occasioned by the presence, in the liquid undergoing examination, of sulphoxyarsenic acid, and not, as was thought, by the presence of free sulphuretted hydrogen.

I have found, indeed, that very dilute solutions of sulphoxy-arsenic acid, even when exposed to the air and light, will keep for a long time. A dilute solution of the acid which had stood for over a month, still gave the silver reaction with a considerable degree of sharpness. Before testing with the silver solution, I was of course careful to remove with asbestus all sulphur which had separated.

One will undoubtedly be here reminded of the extreme difficulty so often experienced in precipitating with sulphuretted hydrogen the last trace of arsenic as sulphide from an acidified solution of arsenic acid. The directions usually given for precipitating arsenic with sulphuretted hydrogen from solutions of arsenic acid are, to acidify strongly with hydrochloric acid, heat to boiling, saturate with the gas, and let the liquid so treated stand in a warm place until all smell of sulphuretted hydrogen has disappeared. Now, as my experiments go to show, unless the gas be passed for many hours, the liquid, after standing until all smell of sulphuretted hydrogen has disappeared, will contain large quantities of sulphoxyarsenic acid. If a portion of such a liquid as that here referred to be filtered and tested with sulphuretted hydrogen, a precipitate of trisulphide of arsenic is almost sure to result, and if the rest be allowed to stand, especially in a warm place, the chances are that it will slowly cloud up, sulphur will be deposited, and more arsenious acid will be formed. If a portion be now tested with sulphuretted hydrogen, a heavier precipitate of tri-sulphide of arsenic will appear.

It will be at once seen how admirably the presence and mode of decomposition of the sulphoxyarsenic acid, as represented in the following equation:

$$2(H_2AsO_3.S) = As_2O_3 + 3(H_2O) + 2S,$$
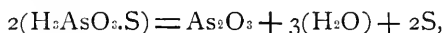
accounts for the sluggish precipitation of the arsenic with sulphuretted hydrogen from an acidified solution of arsenic acid, and how satisfactorily it explains the formation, when the current of gas is slow, of the mixture of pentasulphide, trisulphide, and sulphur.

Recapitulation.

When sulphuretted hydrogen acts upon an *acidified* solution of arsenic acid, the end-products are either: *A.* sulphoxyarsenic acid; *B.* pentasulphide of arsenic; or *C.* a mixture of pentasulphide of arsenic, trisulphide of arsenic, and sulphur.

A. Sulphoxyarsenic acid is the end-product.—This will be the case provided the amount of sulphuretted hydrogen which has acted on the arsenic acid is, in comparison with the amount of arsenic acid in the dilute solution, extremely small (McCay).

$$(1)\ H_3AsO_4 + H_2S = H_3AsO_3.S + H_2O.$$
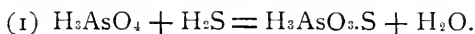
B. Pentasulphide of arsenic is the end-product.—This will be
the case provided the solution of arsenic acid be kept saturated
with sulphuretted hydrogen. We can here distinguish four cases :
a. pentasulphide of arsenic is alone formed provided the solu-
tion of arsenic acid be kept hot and a rapid stream of sulphu-
retted hydrogen be passed through it for a long time (Bunsen) ;
b. the pentasulphide will be alone formed provided the solution
of arsenic acid be brought into a bottle, the bottle almost filled
with freshly boiled cold water, the liquid saturated with sulphu-
retted hydrogen, and the whole, after the bottle has been tightly
corked, placed in a bath of boiling water for one hour (McCay) ;
c. the pentasulphide will be alone formed provided the cold
solution of arsenic acid be treated with a rapid stream of sulphu-
retted hydrogen for an indefinitely long time (Brauner and
Tomiček) ; and *d.* the pentasulphide will be alone formed pro-
vided the cold solution of arsenic acid be brought into a bottle, the
bottle almost filled with pure water, the liquid saturated with
sulphuretted hydrogen, and the whole, after the bottle has been
tightly stoppered, permitted to stand for two weeks (McCay). I
offer the following figures as a proof of this last statement :

Solution used, 25 grams of H_2KAsO_4 in 2000 cc. H_2O.

	Taken.	Calculated.	Found.
1.	25 cc. Standard H_2KAsO_4	$= 0.2670$ gram As_2S_5.	0.2675 gram As_2S_5.
2.	25 cc. Standard H_2KAsO_4	$= 0.2670$ " "	0.2669 " "
3.	50 cc. Standard H_2KAsO_4	$= 0.5340$ " "	0.5350 " "

$$(1) \quad H_3AsO_4 + H_2S = H_3AsO_3.S + H_2O.$$
$$(2) \quad 2H_3AsO_3.S + 3H_2S = As_2S_5 + 6H_2O.$$
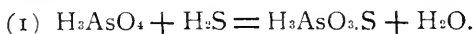
*C. A mixture of pentasulphide of arsenic, trisulphide of arsenic,
and sulphur, is the end-product.*—This will be the case provided the
warm or cold solution of arsenic acid be not saturated, or saturated
but not kept saturated, with sulphuretted hydrogen. Here we have
far more sulphuretted hydrogen than in *A*, but not nearly so much
as in *B*. The solution may be heated, say to 70° C., and a very
slow current of the gas passed into it for a long or short time. Here
then would result, owing to the heat, a constant and rapid loss of
gas. The liquid as a whole is never saturated ; or the solution
may be saturated with sulphuretted hydrogen, and then allowed

to stand. A continuous escape of gas would ensue, and the liquid would soon lose its original strength. The rate of loss of gas by volatilisation is greater than the rate of formation of the penta-sulphide. The solution, in a word, does not remain saturated. It must always be borne in mind that, to obtain the pentasulphide alone, the solution of arsenic acid must be kept saturated with sulphuretted hydrogen. In both cases then, there being no con-stant excess of gas, the conditions for the formation, temporary existence, and decomposition of the sulphoxyarsenic acid are favorable. The formation of the mixture may be imagined to take place in the following way : The sulphuretted hydrogen first acts upon the arsenic acid, changing it to sulphoxyarsenic acid. The sulphoxyarsenic acid, moreover, at those points in the liquid where the gas is in excess—at the point where the gas enters and about the surfaces of the ascending bubbles of gas—is changed slowly to *pentasulphide* of arsenic, and precipitated as such. At other points in the liquid, however, where there is a lack of gas— say, perhaps, to mention only one, along the side of the beaker farthest from the end of the delivery tube—the sulphoxyarsenic acid decomposes, in part, into arsenious acid, water, and *sulphur*. The arsenious acid is then acted upon by the sulphuretted hydrogen and precipitated as the *trisulphide*.

I maintain that there is no reduction of arsenic acid, by sulphur-etted hydrogen, to arsenious acid. The trisulphide found in the mixture is the result of the splitting up of the sulphoxyarsenic acid into arsenious acid, water, and sulphur, and the precipitation of the former as trisulphide by sulphuretted hydrogen.

$$(1) \quad H_3AsO_4 + H_2S = H_3AsO_3.S + H_2O ;$$
$$(2) \quad 2H_3AsO_3.S + 3H_2S = As_2S_5 + 6H_2O ;$$
$$(3) \quad 2H_3AsO_3.S + 6HCl = As_2Cl_6 + 6H_2O + 2S ;$$
$$(4) \quad As_2Cl_6 + 3H_2S = As_2S_3 + 6HCl.$$

Conclusion.

In closing, I call especial attention to the interesting character of sulphoxyarsenic acid, whose ability to exist in the free state has now, I trust, been amply demonstrated. Whether this acid is the same as that corresponding to the several sodium salts prepared by K. Preis, I cannot at present say. Preis mentions but one char-acteristic reaction, which is, that solutions of the salts, when saturated with hydrochloric acid and boiled, decompose, with separation of

pentasulphide of arsenic. This reaction is not given by sulphoxy-arsenic acid or sulphoxyarseniate of potassium prepared as above described. The solutions of this acid are, as I have repeatedly shown, decomposed when boiled with an acid, but into arsenious acid, water, and sulphur. Can it be that Preis's salts are isomorphic mixtures of sodium arseniate and sodium sulpharseniate? The reaction with hydrochloric acid would indicate such a possibility. The point is an important one and worthy of further investigation. I regret to say that I have been unable to consult Preis's original article. My information respecting his work has been obtained from an abstract from the *Chemiké Listy* which appeared in the Repertorium of the *Chemiker Zeitung*, 1888, 23, 73. In regard to this matter I hope to have more to say before long.

JOHN C. GREEN SCHOOL OF SCIENCE,
        PRINCETON, N. J., *June* 1, 1888.

ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.[1]

BY W. A. NOYES.

V.

In a previous paper[2] it has been shown that when the three nitro-toluenes are oxidised in exactly the same manner by an alkaline solution of potassiun ferricyanide, the para and ortho compounds are converted into nitro-benzoic acids with much greater ease than the meta compound. In conclusion, the opinion was expressed that in potassium ferricyanide would be found an agent by means of which a methyl group which is ortho to a nitro group in a benzene derivative can be oxidised, while a methyl group which is meta to the same nitro group is left unoxidised. Experiments to test the correctness of this view were commenced

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[1] Since the manuscript of this article left my hands, two articles, by St. Niementowski (Ber. d. chem. Ges. **21**, 1534), and by St. Niementowski and Br. Rosanski (*ibid.* **21**, 1992), have been received, which cover, in part, the same ground. They give the melting point of β-nitro-p-toluic acid as 161°, a little lower than found by myself. The barium salt is reported as containing 4H$_2$O, but it was precipitated by alcohol, while mine was crystallised from water. Their calcium salt is reported as without water of crystallisation, though for some reason which is not apparent, the salt was dried at 120°. In other respects their results agree essentially with mine.

[2] This Journal **7**, 149.

soon afterwards, but, owing to a variety of causes, the work has been much delayed.

The substance naturally chosen for study was nitro-para-xylene, since it contains one methyl group in the ortho and a second in the para position with reference to the nitro group. The oxidation was at first attempted with a nitro-para-xylene obtained from Kahlbaum. This boiled from 234° to 244° and chiefly from 235°–240°. It gave a mixture of acids from which it was almost impossible to separate any pure substance. It is, perhaps, of some interest to notice, in passing, that one of the products of oxidation seemed to be terephthalic acid. Landolph[1] and Fittica[2] oxidised substances which they supposed to be nitrocymene, with chromic acid, and obtained acids which they called β and γ-nitro-para-toluic acids. These sublimed without melting at a temperature above 300°. Since von Gerichten[3] has shown that the β-nitro-cymene used was not a nitro-cymene at all, and since Widman and Bladin[4] have shown that nitro-cymene cannot be obtained by the method used by Landolph and Fittica, it seems at least probable that the so-called β-nitro-para-toluic acid was in reality terephthalic acid. That the true β-nitro-para-toluic acid has entirely different properties from those of either of the acids obtained by Fittica, will be shown farther on.

For the experiments which were finally successful, nitro-para-xylene was prepared from pure para-xylene by nitrating it with a cooled mixture of nitric acid (sp. gr. 1.40), with a little more than twice its weight of conc. sulphuric acid. The nitration was conducted essentially as described by Nölting and Forel.[5] The nitro-xylene obtained was thoroughly washed with caustic soda, and was distilled two or three times with water vapor. The first and last portions were kept separate from the rest. Lazarus[6] has shown that by distillation with water vapor a hydrocarbon can be almost quantitatively separated from a nitro compound. For small quantities the method is certainly very much better than ordinary fractional distillation. The nitro-xylene obtained in this way, after drying, boiled entirely between 235° and 240°, and fully three fourths of it from 237° to 238° (uncor.). This portion was used for the experiments described below.

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[1] Ber. d. chem. Ges. **6**, 937.   [2] Ibid. **7**, 1357, and Ann. Chem. (Liebig) **172**. 316.
[3] Ibid. **11**, 1092.   [4] Ber. d. chem. Ges. **19**, 584.   [5] Ibid. **18**, 2680.   [6] Ibid. **18**, 578.

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Oxidation of Nitro-para-xylene.

The oxidation was conducted essentially as described in former papers. From 4 to 7 cc. of the nitro-xylene were boiled for three or four hours with 100 grams of potassium ferricyanide, 40 grams of caustic potash, and 400 cc. of water. The oxidation was conducted on a sand-bath in a flask closed with a cork in which was fitted a piece of combustion tubing about one meter long, to act as a condenser. At the end of three or four hours the nitro-xylene which remained unoxidised was distilled off with water vapor. It was then used for a second oxidation. The solution remaining in the flask was filtered and allowed to cool till the potassium ferrocyanide had crystallised as far as possible. The solution was then acidified with hydrochloric acid and extracted with ether. The acids were then converted into the barium salts, but the attempt to separate pure salts from the mixture was not successful.

The separation and identification of the products of oxidation were finally effected by a different method of treating the solution from which the potassium ferrocyanide had been crystallised. To this was added enough hydrochloric acid to render the solution only very slightly acid. This seems to set free chiefly the monobasic acid, and on extracting with ether, a product was obtained which could be easily purified by crystallising two or three times from hot water.

The purified substance proved to be β-nitro-para-toluic acid. It crystallised in fine needles which retain a slight yellow color. It melts at $164°$–$165°$ (cor.) It is easily soluble in hot water, more difficultly soluble in cold water, easily soluble in alcohol and ether.

The analyses were as follows :

I. 0.1096 gram of the acid gave 0.00812 gram N.

II. 0.2163 gram of the acid gave 0.4192 gram CO_2 and 0.0754 gram H_2O.

	Calculated for $C_6H_3 {<} {\,CO_2H \atop \,NO_2 \atop \,CH_3}$.		Found.	
		I.		II.
N	7.73	7.50		...
C	53.04	...		52.86
H	3.87	...		3.87

The copper salt of the acid was also prepared by adding a hot solution of the calcium salt to a solution of copper chloride. The salt separated in microscopic crystals having a bright green color and almost insoluble in hot or cold water. As will be seen later,

the normal copper salt of the isomeric nitro-para-toluic acid consists of blue needles containing four molecules of water. The analysis of the salt was as follows:

0.0560 gram of the salt lost 0.0025 gram H_2O at 170° and gave 0.0101 gram CuO.

$$\left(C_6H_3 {\small\begin{array}{l} \diagup CO_2 \\ - NO_2 \\ \diagdown CH_3 \end{array}} \right)_2 Cu + H_2O.$$

			Found.
$(C_8H_6O_4)_2$	360.	...	...
Cu	63.3	14.34	14.40
H_2O	18.	4.08	4.46

441.3

The method of preparing β-nitro-para-toluic acid which has been described is tedious and the yield is small. In view of the work of Fittica which has been referred to, it seemed of interest to prepare the acid in sufficient quantity for a more careful study of its properties. Sandmeyer[1] has given us a method by which the preparation of the acid is comparatively easy.

The substance necessary for the synthesis of the acid is nitro-para-toluidine, $C_6H_3 {\small\begin{array}{l} \diagup CH_3 \ 1. \\ - NO_2 \ 3. \\ \diagdown NH_2 \ 4. \end{array}}$, (melting point 116°). This was prepared by the method of Gattermann,[2] slightly modified. Para-toluidine was boiled for four or five hours with about twice its weight of glacial acetic acid. The solution was poured into water, and the precipitated acettoluide was washed and dried. 32 grams of this para-acettoluide were added quite rapidly to a mixture of 118 cc. of nitric acid (sp. gr. 1.40), with 47 cc. of sulphuric acid (sp. gr. 1.84). The mixture was vigorously stirred and placed in cold water, so that the temperature varied between 30° and 40° during the addition of the acettoluide. The solution was allowed to stand for fifteen minutes, and was then poured carefully in about 700 cc. of water. The precipitated nitro-acettoluide was filtered with a D. O. Witt filtering plate, washed, and pressed together on the plate to remove as much as possible of the water. It then weighed, in moist condition, 82 grams, and was at once put into a flask with 75 cc. of strong alcohol. The mixture was heated on the water-bath till solution was nearly complete, and then 16 grams of caustic potash dissolved in 20 cc. of water were carefully added. The heating was continued for 15 to 20 minutes. The solution

[1] Ber. d. chem. Ges. **18**, 1492.   [2] Ibid. **18**, 1482.

was then cooled rapidly, and the nitro-toluidine which separated was filtered off and washed with alcohol of 30 per cent. The nitro-toluidine obtained in this way seemed to be perfectly pure and weighed 27.5 grams. By the method described, para-toluidine yields somewhat more than its own weight of nitro-toluidine, and the preparation requires but little time.

Nitrile of β-Nitro-para-toluic Acid.

The conversion of the nitro-toluidine into the cyanide was conducted as described by Sandmeyer.[1] A somewhat larger amount of potassium cyanide was used, however, in order to prevent the separation of cuprous cyanide at the end of the reaction. The solution of cuprous cyanide was prepared by adding carefully a solution of 33 grams of potassium cyanide to a hot solution of 28 grams of crystallised copper sulphate in about 150 cc. of water. 15.2 grams of the finely powdered nitro-toluidine were put in a flask with 500 cc. of cold water. 8.6 grams of potassium nitrite and 26 cc. of hydrochloric acid (sp. gr. 1.128) were added, the flask was corked, and the mixture shaken vigorously for ten minutes. The diazo compound which was formed remained dissolved, and the solution was filtered quickly from a small portion of the nitro-toluidine which remained unconverted. The latter, if washed at once with water, is pure enough for use in a second operation. The solution containing the diazo compound has a light permanganate red color, caused apparently by a slight decomposition. The solution containing the cuprous cyanide was placed over a vigorous flame and kept at a temperature of about 70°, while the diazo solution was added as rapidly as it could be without lowering the temperature too much. At the temperature mentioned, the cyanide formed separates as a yellowish brown solid, while, if the temperature is slightly higher, it separates as a dark colored oil which is apparently less pure. When the reaction was complete the solution was cooled rapidly and the cyanide was filtered off at once. The yield is very good, and the product is pure enough for conversion into the acid.

For analysis the cyanide was crystallised once or twice from hot water. On cooling the hot solution it separates in fine needles which when pure are almost white, but which usually have a light yellow color. It is moderately soluble in ether, and separates, on

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[1] Loc. cit.

spontaneous evaporation of the solution, in short thick prisms. It is easily soluble in alcohol. It melts at 100°. 0.1234 gram of the substance gave 0.0217 gram of N, which corresponds to 17.59 per cent. Theory requires 17.29 per cent.

β-Nitro-para-toluic Acid.

Sandmeyer saponified the cyanides of the nitro compounds with which he worked by boiling with an aqueous solution of caustic soda. The same method applied to this cyanide caused the formation of a mixture of substances from which it was almost impossible to separate anything in pure condition. Good results were obtained, however, by heating in sealed tubes with concentrated hydrochloric acid. From ten to fifteen parts of the acid were used to one of the cyanide, and the heating was continued from one to two hours at a temperature of 150° to 160°. On cooling, the portion which had passed into solution separated in long and rather thick needles which were almost perfectly white. The acid was purified by solution in dilute ammonia, filtering, precipitating with hydrochloric acid, and recrystallising from hot water. The pure acid melted at 164°–165° (cor.), and had the same properties as those of the acid obtained by the oxidation of nitro-xylene with potassium ferricyanide.

Barium β-Nitro-para-toluate, $\left(C_6H_3 {\overset{\displaystyle CO_2}{\underset{\displaystyle CH_3}{-NO_2}}} \right)_2 Ba + 5H_2O.$—The

barium salt was prepared in the usual way. It is easily soluble in water, and has a tendency to form supersaturated solutions. On cooling a hot, moderately concentrated solution, it separates in crystals radiating from centers and forming half-balls on the bottom of the beaker or top of the liquid. If very concentrated, the solution is converted into a solid mass of crystals. The salt, as it at first separates, seems to contain *nine and one-half* molecules of water. Two analyses of a salt air-dried for a short time gave, respectively, 25.53 and 25.99 per cent. of water. Theory requires for 9½ molecules 25.60 per cent. A salt by a new crystallisation, and which was dried by pressing between filter paper, gave but 21.33 per cent. of water, however, and when air-dry for two or three days in a rather warm room, the salt contains but *five* molecules of water. The salt loses its water slowly but almost completely over sulphuric acid. The other determinations of water were as follows:

I. 0.1607 gram of the salt air-dried for two days lost 0.0247 gram H_2O at 135°.

II. 0.4103 gram of the salt air-dried for 28 hours in a warm room lost 0.0647 gram H_2O at 135°.

III. 0.1722 gram of a salt which was allowed to stand over sulphuric acid with very frequent weighings till a point was reached when it ceased to lose weight rapidly, lost 0.0272 gram H_2O at 135°.

	Calculated for $\left(C_6H_3 \overset{\diagup CO_2}{\underset{\diagdown CH_3}{-NO_2}}\right)_2 Ba + 5H_2O.$	I.	Found. II.	III.
$5H_2O$	15.33	15.37	15.77	15.80

The determinations of barium were as follows :

I. 0.2054 gram of the dry salt gave 0.0961 gram $BaSO_4$.
II. 0.1788 gram of the dry salt gave 0.0832 gram $BaSO_4$.
III. 0.1896 gram of the dry salt gave 0.0882 gram $BaSO_4$.

	Calculated for $\left(C_6H_3 \overset{\diagup CO_2}{\underset{\diagdown CH_3}{-NO_2}}\right)_2 Ba.$	I.	Found. II.	III.
$(C_8H_6NO_4)_2$	3.60	...	...	...
Ba	1.37	27.56	27.51	27.37	27.36

Calcium β-Nitro-para-toluate, $\left(C_6H_3 \overset{\diagup CO_2}{\underset{\diagdown CH_3}{-NO_2}}\right)_2 Ca + 2H_2O.$—The calcium salt is much more difficultly soluble than the barium salt. It seems to be about equally soluble in hot and cold water. By evaporating on the water-bath, the salt is deposited from the hot solution in needles. If these are filtered off, the filtrate deposits nothing on cooling. The same salt separates by the spontaneous evaporation of the cold solution, forming a network of needles which creep up and cover the walls of the beaker. This property is very characteristic of the salt. In determining the water of crystallisation it was found that the salt melted partially at 170°. Heated rapidly in a capillary tube it forms a glossy mass at 180°–185°, but does not become entirely liquid.

The analyses were as follows :

I. 0.1786 gram of the salt deposited by the hot solution lost 0.0148 gram H_2O at 170°, and gave 4.0550 gram $CaSO_4$.

II. 0.2173 gram of the salt deposited by the cold solution lost 0.0175 gram H_2O at 170°, and gave 0.0672 gram $CaSO_4$.

Calculated for

$$\left(C_6H_3{\overset{\diagup CO_2}{\underset{\diagdown CH_3}{-NO_2}}}\right)_2 Ca + 2H_2O.$$

			Found.	
			I.	II.
$(C_8H_6NO_4)_2$	360	...	...	...
Ca	40	9.17	9.06	9.10
$2H_2O$	36	8.26	8.29	8.05
	436			

Copper β-Nitro-para-toluate, $\left(C_6H_3{\overset{\diagup CO_2}{\underset{\diagdown CH_3}{-NO_2}}}\right)_2 Cu + H_2O.$—This
was prepared by adding a solution of the calcium salt to a solution of copper chloride. It separates at first as an amorphous precipitate, but on warming it is quickly converted into microscopic crystals of a bright green color. This salt is the most characteristic of any of those prepared. It is especially suited to distinguish the acid from the well known α-nitro-para-toluic acid.

I. 0.1051 gram of the salt lost 0.0045 gram H_2O at 160°–170° and gave 0.0188 gram CuO.

II. 0.1619 gram of the salt lost 0.0070 gram H_2O at 168° and gave 0.0290 gram CuO.

Calculated for

$$\left(C_6H_3{\overset{\diagup CO_2}{\underset{\diagdown CH_3}{-NO_2}}}\right)_2 Cu + H_2O.$$

			Found.	
			I.	II.
$(C_6H_6NO_4)_2$	360	...	...	...
Cu	63.3	14.34	14.34	14.36
H_2O	18	4.08	4.28	4.33
	441.3			

β-Amido-para-toluic Acid.—This was prepared by reducing the acid with tin and hydrochloric acid. After diluting, precipitating the tin with hydrogen sulphide, and evaporating to a small volume, the chloride of the new acid separated in fine needles, on cooling the strongly acid solution. These were washed with hydrochloric acid of sp. gr. 1.12, in which they were difficultly soluble. After drying, the free acid was obtained by warming the chloride with somewhat less than the calculated amount of very dilute ammonia, cooling and filtering.

As thus obtained, the acid is white and apparently amorphous. It may be obtained in very fine leaflets or plates by crystallising from hot water, but these usually have a brownish color. The acid is difficultly soluble in cold and hot water, easily soluble in

alcohol. Its aqueous solution shows a blue-violet fluorescence, which disappears on adding a strong acid, but returns on adding ammonia. The same fluorescence is shown by the salts. The acid melts at 177°–178° (cor.), and at the same time decomposes with the evolution of a gas. The analyses of the acid were as follows:

I. 0.1312 gram of the acid gave 0.01226 gram N.
II. 0.1335 gram of the acid gave 0.01236 gram N.

	Calculated for $C_6H_3{-}\genfrac{}{}{0pt}{}{CO_2H}{CH_3}^{NH_2}$	Found.	
		I.	II.
N	9.27	9.34	9.26

Barium β-Amido-para-toluate, $\left(C_6H_3{-}\genfrac{}{}{0pt}{}{CO_2}{CH_3}^{NH_2}\right)_2 Ba + 4H_2O.$ —

This was prepared as usual by boiling the acid with barium carbonate. It separates, on cooling a hot solution, in brown leaflets or scales which are very difficultly soluble both in hot and cold water. It was not found possible to determine the water of crystallisation directly, as the salt loses only three or four per cent. of water at temperatures below that at which it begins to decompose. The determinations of barium were as follows:

I. 0.1935 gram of the salt gave 0.0885 gram $BaSO_4$.
II. 0.2093 gram of the salt gave 0.0969 gram $BaSO_4$.

	Calculated for $\left(C_6H_3{-}\genfrac{}{}{0pt}{}{CO_2}{CH_3}^{NH_2}\right)_2 Ba + 4H_2O.$		Found.	
			I.	II.
$(C_8H_8NO_2)_2$	300	...	...	...
Ba	137	26.92	26.90	27.23
$4H_2$	72	14.14	...	...
	509			

Calcium β-Amido-para-toluate, $\left(C_6H_3{-}\genfrac{}{}{0pt}{}{CO_2}{CH_3}^{NH_2}\right)_2 Ca + 2H_2O.$ —

The attempt to prepare the calcium salt in the usual way, by boiling the acid with calcium carbonate, gave a solution which was acid in reaction. Accordingly the solution was boiled with a slight excess of thin milk of lime, and the excess of lime was precipitated with carbon dioxide. The salt separates in scales which have a slight brown color. The salt loses most of its water at 135°, but there is a slight additional loss at 200°.

The analyses were as follows:

I. 0.1646 gram of the salt lost 0.0157 gram H_2O at 200° and gave 0.0591 gram $CaSO_4$.

II. 0.2034 gram of the salt lost 0.0191 gram H_2O at 200° and gave 0.0729 gram $CaSO_4$.

	Calculated for $\left(C_6H_3{\displaystyle {\overset{CO_2}{\underset{CH_3}{-NH_2}}}} \right)_2 Ca + 2H_2O.$		I. Found.	II.
$(C_8H_8NO_2)_2$	300	...	...	...
Ca	40	10.64	10.56	10.54
$2H_2O$	36	9.57	9.54	9.39
	376			

Copper β-Amido-para-toluate, $\left(C_6H_3{\displaystyle {\overset{CO_2}{\underset{CH_3}{-NH_2}}}} \right)_2 Cu.$—This is obtained as an amorphous, light green precipitate when a solution of copper chloride is added to a solution of the calcium salt. It is almost insoluble in hot or cold water. When air-dry the salt still retains a small amount of water, which it loses at 135°.

I. 0.1037 of the salt dry at 135° gave 0.0223 gram CuO.

II. 0.1061 gram of the salt dry at 135° gave 0.0231 gram CuO.

	Calculated for $\left(C_6H_3{\displaystyle {\overset{CO_2}{\underset{CH_3}{-NH_2}}}} \right)_2 Cu.$		I. Found.	II.
$(C_8H_8NO_2)_2$	300	...	...	...
Cu	63.3	17.42	17.15	17.39
	363.3			

Constitution of β-Amido-para-toluic Acid.

There could be scarcely a question as to the constitution of the nitro and amido-toluic acids which have been described. It was of some interest, however, in view of the work of Fittica, which has been referred to, to furnish a direct proof of the structure by converting the amido acid into a known oxy-toluic acid. For this purpose, about 40 milligrams of the acid were dissolved by shaking with dilute sulphuric acid and a little more than the calculated amount of potassium nitrite. On boiling the solution and cooling, the oxy-acid separated in needles. After boiling with a little bone-black and crystallising from hot water, these were nearly white and melted at 177° (cor.). The acid also gives a violet color with ferric

chloride. These properties are sufficient to characterise it as
β-oxy-para-toluic acid, $C_6H_3\begin{smallmatrix}\diagup CO_2H \;\; 1. \\ -OH \quad 2. \\ \diagdown CH_3 \quad 4.\end{smallmatrix}$, and the nitro and amido
acids must have a similar constitution. It seems almost certain,
therefore, that the true β-nitro-para-toluic acid has been described
here for the first time, and that the acids prepared by Landolph
and Fittica were not nitro-toluic acids.

Nitrile of α-Nitro-para-toluic Acid.

The copper salt of α-nitro-para-toluic acid seems never to have
been prepared. A comparison of the salt with that of the β-acid
seemed of interest. The acid itself was prepared from nitro-para-
toluidine, $C_6H_3\begin{smallmatrix}\diagup CH_3 \;\; 1. \\ -NO_2 \; 2. \\ \diagdown NH_2 \; 4.\end{smallmatrix}$ (melts at 78°), by the same method which
has been described for the isomeric acid. The cyanide obtained
separates at first as a coffee-brown precipitate. It crystallises from
a hot aqueous solution in fine white needles which melt at 107°. A
determination of nitrogen in the substance gave 17.44 per cent. of
N. Theory requires 17.29 per cent. The nitrile was converted
into the acid by heating with concentrated hydrochloric acid in
sealed tubes, and the calcium salt was prepared in the usual way.

Copper α-Nitro-para-toluate, $\left(C_6H_3\begin{smallmatrix}\diagup CO_2 \\ -NO_2 \\ \diagdown CH_3\end{smallmatrix} \right)_2 Cu + 4H_2O.$ —

When a solution of the calcium salt is added to a hot solution of
copper chloride, a light blue amorphous precipitate is obtained
which, after washing with hot water, consists of a basic salt of some-
what varying composition. The salt may be dried at 135° without
change of color. If it is then heated to 200° it turns green and
loses about two per cent. in weight. In two cases the salts gave
amounts of water and copper which agree fairly well with the
formula $Cu_3\left(C_6H_3\begin{smallmatrix}\diagup CO_2 \\ -NO_2 \\ \diagdown CH_3\end{smallmatrix} \right)_4 (OH)_2 + H_2O$. A third salt gave a
larger per cent. of copper. A fourth gave 42.72 per cent. of carbon,
3.11 per cent. of hydrogen, and 17.01 per cent. of copper. A salt
of the formula $Cu_3\left(C_6H_3\begin{smallmatrix}\diagup CO_2 \\ -NO_2 \\ \diagdown CH_3\end{smallmatrix} \right)_5 OH + H_2O$ requires 42.67 per
cent. carbon, 2.93 per cent. hydrogen, and 16.88 per cent. copper.

The filtrate from the basic salt deposits the normal salt, on

cooling, in the form of bright blue needles mixed with white crystals of the acid. The latter can be easily removed by means of ether. The same salt may be obtained more easily by dissolving 0.4 gram of the calcium salt in 100 cc. of hot water, with the addition of 0.01 gram of hydrochloric acid, and adding 0.2 gram of copper chloride dissolved in 100 cc. of hot water. On filtering and cooling, the salt is deposited as before, in the form of beautiful blue needles.

The analyses were as follows :

I. 0.0991 gram of the salt lost 0.0139 gram H_2O at 135° and gave 0.0159 gram CuO.

II. 0.1591 gram of the salt lost 0.0230 gram H_2O at 135° and gave 0.0253 gram CuO.

	Calculated for $\left(C_6H_3\genfrac{}{}{0pt}{}{\nearrow CO_2}{-NO_2}{\searrow CH_3}\right)_2 Cu + 4H_2O.$		Found. I.	II.
$(C_8H_8NO_4)_2$	360.	...	...	...
Cu	63.3	12.78	12.82	12.70
$4H_2O$	72.	14.54	14.03	14.46
	495.3			

Formation of Nitro-terephthalic Acid.

After removing most of the β-nitro-para-toluic acid from the slightly acidified solution referred to in the early part of this paper, more acid was added, and the solution was extracted again with ether. On recrystallising from hot water the acids obtained, two substances were separated. One of these crystallised in needles aggregated to balls. These melted at 266°–268°, and were evidently nitro-terephthalic acid, which should melt at 270°.[1] The analysis gave 6.75 per cent. of N. Theory requires 6.64 per cent.

The other substance separated in well formed plates. These lose water on heating, and melt at the same temperature as the needles. The analyses of the plates showed that their composition was that of nitro-terephthalic acid, with the addition of two molecules of water. An attempt was made to obtain the same substance by crystallising ordinary nitro-terephthalic acid under various conditions, and with the addition of fragments of the plates ; also by oxidising nitro-para-xylene with a strongly alkaline solution of potassium permanganate, and by oxidising β-nitro-para-

[1] Burkhardt, Ber. d. chem. Ges. **10**, 145.

toluic acid with potassium ferricyanide. All of these attempts
were unsuccessful, and the only method by which the plates could
be obtained was by oxidising the nitro-para-xylene with potassium
ferricyanide. They were obtained repeatedly in that way.

These results seem to indicate that the water which the sub-
stance loses on heating is not water of crystallisation, but water of
constitution. If that is true, the probable formula of the substance
is $C_6H_3—NO_2\begin{smallmatrix} \diagup C(OH)_3 \\ \diagdown C(OH)_3 \end{smallmatrix}$. The temporary existence of such a substance
as the result of oxidation is entirely in accordance with the views
ordinarily held with regard to the oxidation of hydrocarbon resi-
dues. The more permanent existence of the substance in the
present case seems to be analogous to the formation of ortho-
sulphamine acids instead of sulphinides, which has been described
in previous papers.[1] *In both cases potassium ferricyanide seems
to show itself an oxidising agent which resists the formation of
anhydro compounds.* Fahlberg and List[2] have recently expressed
the opinion that the first product of the oxidation of a sulphamide
is a sulphinide, and that the sulphamine acid results from the
action of free alkali on the sulphinide. If that method of action
held in the present case, the substance which I have described
should have been obtained by the oxidation of nitro-para-xylene
with the strongly alkaline solution of potassium permanganate, or
by oxidising nitro-para-toluic acid with potassium ferricyanide.
Neither method gave it. A more natural explanation in the
present case seems to be that the hydrogen of the hydroxyl groups
formed by oxidation is at once replaced by potassium, and that the
presence of the metal resists the formation of an anhydride in the
same manner that it does in carbonates. It seems probable that a
similar explanation holds in the case of the sulphamides. It has
been shown[3] repeatedly that the hydrogen of the sulphamide group
can be replaced by metals, and in the strongly alkaline solution it
is probable that both hydrogen atoms are so replaced. The
presence of the metal might then act to prevent the formation of
the anhydride much as in the case described in the present paper.
This view seems to me more natural than the one proposed by
Fahlberg. It is entirely consistent with the conversion of sulph-

[1] This Journal **8**, 179, and **9**, 94.   [2] Ber. d. chem. Ges. **21**, 244.
[3] Wolkow, Ber. d. chem. Ges. **3**, 424.   This Journal **8**, 181.

inides into sulphamine acids by the action of alkalies, and that is the chief fact brought forward in support of his view.

I am unable to give any explanation as to why the alkaline solution of potassium ferricyanide should act differently from an alkaline solution of potassium permanganate (really containing potassium manganate) as it has been shown to do in this paper.

The analyses of the plates were as follows:

I. 0.1174 gram of the substance gave 0.00677 gram N.

II. 0.0755 gram of the substance lost 0.0110 gram H_2O at 135°.

	Calculated for $C_6H_3-NO_2\begin{smallmatrix}C(OH)_3\\\\C(OH)_3\end{smallmatrix}$	Found.	
		I.	II.
N	5.67	5 77	...
$2H_2O$	14.57	...	14.19

Oxidation of Mono-nitro-meta-xylene.

Nitro-meta-xylene (from Kahlbaum) was oxidised in the same manner as the nitro-para-xylene. The acids obtained were converted into the barium salts, and from these the salt of a bibasic acid was easily separated in pure condition. A small amount of a more easily soluble salt was also formed, but attempts to purify it were not successful. Its presence indicates the formation of a small amount of a monobasic acid. The oxidation of nitro-meta-xylene takes place much more easily than that of nitro-para-xylene. The oxidation of nitro-meta-xylene can be effected still more easily with potassium permanganate and the same acid is formed.

β-Nitro-isophthalic Acid.

The acid was separated from the purified barium salt by warming it with a slight excess of very dilute hydrochloric acid till it passed into solution. On cooling the solution the acid separated in small granular crystals having a slight yellow color. Under a good glass the crystals were seen to consist of very small, short needles.

The analysis was as follows:

0.1048 gram of the acid gave 0.00686 gram N.

| | Calculated for $C_6H_3-CO_2H\begin{smallmatrix}CO_2H\\\\NO_2\end{smallmatrix}$ | Found. |
| N | 6.64 | 6.54 |

The acid obtained by oxidation with potassium ferricyanide

melts at 257°–258° (cor.). That obtained by oxidation with potassium permanganate melts at 258°–259°. The acid is easily soluble in hot water, more difficultly soluble in cold water. It seems to be identical with the β-nitro-isophthalic acid which is formed in small amount when isophthalic acid is treated with fuming nitric acid,[1] and which melts at 260°. Beyer does not seem to have established the constitution of his acid, probably because he obtained it in too small amount. Since Harmsen[2] has shown that the asymmetric nitro-meta-xylene is formed when meta-xylene is nitrated, the constitution of the acid must be repre-sented by the formula $C_6H_3$$\begin{smallmatrix}\diagup CO_2H\ 1.\\-CO_2H\ 3.\\\diagdown NO_2\ 4.\end{smallmatrix}$ That this is actually the structure of the acid was established by reducing the acid with tin and hydrochloric acid, and by converting the amido acid obtained into the corresponding oxy acid by Griess' reaction. The asym-metric oxy-isophthalic acid[3] was obtained. It melted with decom-position at 300°–303° (uncor.), and gave an onion-red color with ferric chloride.

Barium β-Nitro-isophthalate, $C_6H_3$$\begin{smallmatrix}\diagup CO_2\\-CO_2\\\diagdown NO_2\end{smallmatrix}$$>Ba+1\tfrac{1}{2}H_2O.$—When the acids which have been referred to are converted into the barium salts, these pass into solution readily and appear to be quite easily soluble. If the solution is evaporated and the salt deposited, how-ever, a considerable amount of water and prolonged heating are necessary to bring it again into solution. The salt is deposited from the hot solution, during evaporation, in small needles or prisms of a light yellow color. The salt loses its water very rapidly and almost entirely on standing over calcium chloride. The salt for the third analysis was from the acid obtained by oxidation with potassium permanganate. The other salts were from the oxidation with potassium ferricyanide.

I. 0.2541 gram of the salt lost 0.0174 gram H_2O at 132° and gave 0.1593 gram $BaSO_4$.

II. 0.2967 gram of the salt lost 0.0205 gram H_2O at 132° and gave 0.1855 gram $BaSO_4$.

III. 0.3242 gram of the salt lost 0.0206 gram H_2O and gave 0.2037 gram $BaSO_4$.

[1] Beyer, J. prakt. Chem. (2) **22**, 352.   [2] Ber. d. chem. Ges. **13**, 1558.
[3] Remsen and Iles, this Journal **1**, 132.

	Calculated for $C_6H_3-\overset{/CO_2}{\underset{\diagdown NO_2}{\overset{\mid}{CO_2}}}\!\!>\!Ba +1\tfrac{1}{2}H_2O.$		I.	Found. II.	III.
$C_8H_3NO_6$	209	...	...	...	...
Ba	137	36.73	36.86	36.76	36.95
$1\tfrac{1}{2}H_2O$	27	7.24	6.85	6.91	6.35
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ANALYSIS OF SOME SOUTHERN FRUITS WITH REFERENCE TO THEIR FOOD VALUES.

By Charles L. Parsons.

König, in his well known work, " Nahrungs- und Genussmittel," gives a summary of all published analyses of fruits,[1] their nutritive ratio and food units. This summary contains the analyses of a large number of fruits, but singularly enough, but one analysis of oranges is given, and that was made previously to the investigation by Buignet, in which the existence of cane sugar in acid fruits was conclusively proved.[2]

Of late years oranges have become so important both as a food and a luxury, and have become so great a source of wealth to some of our Southern States, especially Florida, that I decided to make food analyses of the prominent varieties grown in that State. I have also made analyses of pomegranates and persimmons, which, although seldom seen in the Northern markets, still form no inconsiderable part of the fruits of the South.

For my purpose I obtained direct from a friend in Oviedo, Florida, a box containing eight different varieties of oranges fresh from the grove. The oranges were carefully labeled, and each wrapped in tissue paper. The pomegranates and persimmons were obtained from Hawkinsville, Georgia. I commenced work on the fruits as soon as they arrived. For the analyses a number of oranges were taken of each variety ; total acids and water determined in an average sample of the fresh fruit, and the remainder of the pulp dried at about 95° C. Pomegranates and persimmons were treated in the same way, with the exception that the pulp of the persimmons was separated from the seed by means of a large-meshed sieve, previous to drying.

In the following tables I have given a comparison of the dry substance of the fruits analysed, with the dry substance of bread, cocoanut, and banana, giving their nutritive ratio and number of food units. I selected the Navel as a type of the Florida oranges

[1] König, Nahrungs- und Genussmittel, 2d edition, Bd. II, S. 491-497.
[2] Ann. de Chim. et de Phys. [3d series], **61**, 233.

in this comparison, and the Guy Pope, a Messina orange, sold last season in large quantities from New York City, as a type of the Mediterranean orange, of which more than two million dollars' worth are annually imported.

The following results are averages of my analyses :

	H₂O.	Crude Protein	Free Acids.	Glucose Sugar	Cane Sugar.	Ether Ext.	Crude Fibre.	Ash.	Albuminoid Nitrogen.	Nitrogen Free Extract.
Sweet Pomegranates, ...	78.27	1.33	.368	11.61	1.04	1.24	2.63	.761	.177	15.77
Sour Pomegranates,	75.41	1.60	1.85	10.40	.26	2.05	2.83	.544	.203	17.57
Persimmons, . .	66.12	.827	.000	13.54	1.03	.701	1.78	.861		29.711
Fla. Orange, Bitter Sweet	86.86	.815	.417	5.71	.84	.243				
Fla. Orange, Tangerine, ...	83.56	.792	.477	6.00	3.41	.256				
Fla. Orange, Mandarin, ...	79.95	.834	.855	4.77	8.07	.146				
Fla. Orange, Bloods	85.57	.700	.670	5.70	3.94	.100				
" Navels	83.70	1.12	.662	6.03	4.68	.234				
" Russets	83.18	.905	.817	7.29	4.51					
Fla. Orange, Common Florida, . .	86.58	.862	.756	4.60	4.38	.076				
Fla. Orange, Fla. Sour, ...	86.76	1.03	2.55	3.86	.97	.125				
Messina Orange, Guy Pope, . .	86.22	.980	1.18	5.95	1.82	.166				

	Ntg = Protein.	Fat.	Nitrogen—free Extract = N.Ntg.	Nutritive Ratio Ntg:N.Ntg +(1¾×⅟) fat)::1:1.	Food Units in 1 kilo : Ntg : fat:N.Ntg :: 5:3:1.	Nutritive Ratio=Ntg : N.Ntg + N.Ntg + (fat × 1.75) :: 1:—
Bread, ...	10.94	87.97	.71	8.7	1446.2	
Sweet Pomegranates, . .	6.12	72.52	5.70	13.5	1202.2	
Sour Pomegranates, . .	6.50	71.44	8 34	13.4	1289.6	
Persimmons, ...	2.44	90.63	2.07	38.6	1090.4	
Banana, ...	6.94	85.72	2.33	12.9	1274.1	
Solid portion Cocoanut, .	10.31	15.10	67.33	12.9	2686.4	
Mandarin Orange, . . .	4.15	85.88	.73	21.	1088.2	
Navel Orange, ...	6.87	80.85	1.44	12.1	1195.2	
Guy Pope Orange, . . .	5.78	71.11	1.22	12.7	1036.7	

To any one who is acquainted with the flavor and general edibility of the different varieties of Florida oranges, it will be apparent that these analyses indicate that the best varieties contain the highest percentages of cane sugar, and that if the analysed varieties were to be placed in the order of their superior flavor, and in the order of their contents of cane sugar, the two series would be very nearly identical.

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